

Efficient and Convenient Nonaqueous Workup Procedure for the Preparation of Arylboronic Esters

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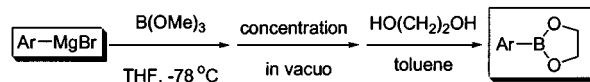
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Abstract: An efficient one-pot synthetic protocol for the synthesis of arylboronic esters has been established. The concentrated addition mixture of trimethylborate with aryl Grignard reagents was treated with low molecular weight diols (ethylene glycol, 1,3-propanediol) and toluene, the corresponding arylboronic esters were isolated in a convenient way with high yields. The diols not only serve as *water replacement* for the workup step, but also as well as the reagent for the preparation of arylboronic esters.

Suzuki cross-coupling reactions of aryl halides and aryl triflates with arylboronic acids have been widely used for the construction of the aryl–aryl bond in modern organic synthesis.¹ Much of the recent endeavors on the Suzuki coupling reaction have been concentrated on the metal ligand system. In particular, new catalyst systems² that facilitate the cross-coupling of the less reactive aryl chlorides with boronic acids have been developed, greatly expanding the scope of the reaction. Some efforts have also been devoted to develop new organoboron reagents. For instance, aryltrifluoroborate salts³ have been demonstrated to be as effective (in some cases better) at coupling with arenediazonium tetrafluoroborates,⁴ diaryliodonium salts,⁵ and aryl triflates⁶ in the presence of Pd catalyst. Despite that, the most popular arylboron derivatives used for Suzuki coupling reactions are arylboronic acids, which could be prepared by reacting a corresponding aryllithium or arylmagnesium complex with trialkylborate, followed by an acidic aqueous workup.⁷ However, the aqueous workup procedure was sometimes troublesome and led to boronic acid only in moderate yield. In addition, the aqueous solution con-

Scheme 1. One-Pot Nonaqueous Workup Synthesis of Arylboronic Esters



taminated with boronic residue is not disposable, making this procedure not environmentally benign for large-scale preparation of the arylboronic acids. On the other hand, arylboronic esters⁸ have been used as a substitution of arylboronic acids to efficiently couple with aryl halides or aryl triflates in the presence of Pd-catalyst. Traditionally, arylboronic esters were prepared by a two-step synthesis:⁹ from aryl halides to arylboronic acids, followed by treating the arylboronic acids with corresponding alcohol or diol in organic solvent. Alternatively, arylboronic esters can be obtained by PdCl₂(dppf)-catalyzed boration of aryl halides or aryl triflates with dialkoxyborane.¹⁰ In this case, a small amount of the dehalogenated product is obtained as the side product. Pd-catalyzed borations of aryl halides or aryl triflates with tetraalkoxydiboron¹¹ are more successful, leading to the formation of arylboronic esters with high yield. A broad range of functional groups are tolerable in these Pd-catalyzed borations makes these methodologies attractive. In addition, Rh-catalyzed aromatic C–H bond activation for the regioselective boration with pinacolborane in an inert solvent also provides the corresponding boronic ester efficiently.¹² However, the dialkoxyborane is hygroscopic and the tetraalkoxydiboron is expensive, thus limiting these catalytic methods to be suitable only for small-scale preparation. Therefore, an environment friendly method for large-scale preparation of arylboronic esters with high efficiency is highly desired. In this paper, we report a convenient one-pot process for the preparation of arylboronic esters.

Arylboronic esters can be prepared by a one-pot procedure as shown in Scheme 1. Aryl bromide and aryl iodide are widely available from the major chemical suppliers at reasonable prices. The transformation from aryl halides to their Grignard reagents with magnesium metal in ethereal solvents (e.g., THF, diethyl ether) has been well documented. At $-78\text{ }^{\circ}\text{C}$, the aryl Grignard reagents formed were added into the THF solution containing an excess amount (2 equiv) of trimethylborate, i.e., B(OMe)₃. The reaction mixture was allowed to return to room temperature by removing the cooling bath, leading to the formation of aryl dimethoxyboronate. Instead of quenching the reaction mixture with acidic aqueous solution, the solvent and the excess amount of B(OMe)₃ were removed by a rotary evaporator at ca. 20

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(1) (a) Miyaura, N.; Suzuki, A. *Chem. Rev.* **1995**, *95*, 2457. (b) Suzuki, A. *J. Organomet. Chem.* **1999**, *675*, 147.

(2) (a) Littke, A.; Fu, G. C. *Angew. Chem., Int. Ed. Engl.* **1998**, *37*, 3387. (b) Old, D. W.; Wolfe, J. P.; Buchwald, S. L. *J. Am. Chem. Soc.* **1998**, *120*, 972. (c) Wolfe, J. P.; Buchwald, S. L. *Angew. Chem., Int. Ed. Engl.* **1999**, *38*, 2413. (d) Singer, R. A.; Buchwald, S. L. *Tetrahedron Lett.* **1999**, *40*, 1095. (e) Zhang, C.; Huang, J.; Trudell, M. L.; Nolan, S. P. *J. Org. Chem.* **1999**, *64*, 3804. (f) Littke, A. F.; Dai, C.; Fu, G. C. *J. Am. Chem. Soc.* **2000**, *122*, 4020. (g) Zapf, A.; Beller, M. *Chem. Eur. J.* **2000**, *6*, 1830.

(3) Vedejs, E.; Chapman, R. W.; Fields, S. C.; Lin, S.; Schrimpf, M. R. *J. Org. Chem.* **1995**, *60*, 3020.

(4) (a) Darses, S.; Genêt, J.-P.; Brayer, J.-L.; Demoute, J.-P. *Tetrahedron Lett.* **1997**, *38*, 4393. (b) Darses, S.; Michaud, G.; Genêt, J.-P. *Eur. J. Org. Chem.* **1999**, 1875.

(5) Xia, M.; Chen, Z.-C. *Synth. Commun.* **1999**, *29*, 2457.

(6) Molander, G. A.; Ito, T. *Org. Lett.* **2001**, *3*, 393.

(7) Diorazio, L. J.; Widdowson, D. A.; Clough, J. M. *Tetrahedron* **1992**, *48*, 8073.

(8) (a) Giroux, A.; Han, Y.; Prasit, P. *Tetrahedron Lett.* **1997**, *38*, 3841. (b) Wang, S.; Oldham, W. J.; Hudack, R. A.; Bazan, G. C. *J. Am. Chem. Soc.* **2000**, *122*, 5695. (c) Kristensen, J.; Lysen, M. Vedso, P. Begtrup, M. *Org. Lett.* **2001**, *3*, 1435.

(9) (a) Longstaff, C.; Rose, M. E. *Org. Mass Spectrom.* **1982**, *17*, 508. (b) Diorazio, L. J.; Widdowson, D. A.; Clough, J. M. *Tetrahedron* **1992**, *48*, 8073.

(10) (a) Murata, M.; Oyama, T.; Watanabe, S.; Masuda, Y. *J. Org. Chem.* **2000**, *65*, 164. (b) Baudoin, O.; Guénard, D.; Guéritte, F. *J. Org. Chem.* **2000**, *65*, 9268.

(11) (a) Ishiyama, T.; Murata, M.; Miyaura, N. *J. Org. Chem.* **1995**, *60*, 7508. (b) Ishiyama, T.; Itoh, Y.; Kitano, T.; Miyaura, N. *Tetrahedron Lett.* **1997**, *38*, 3447.

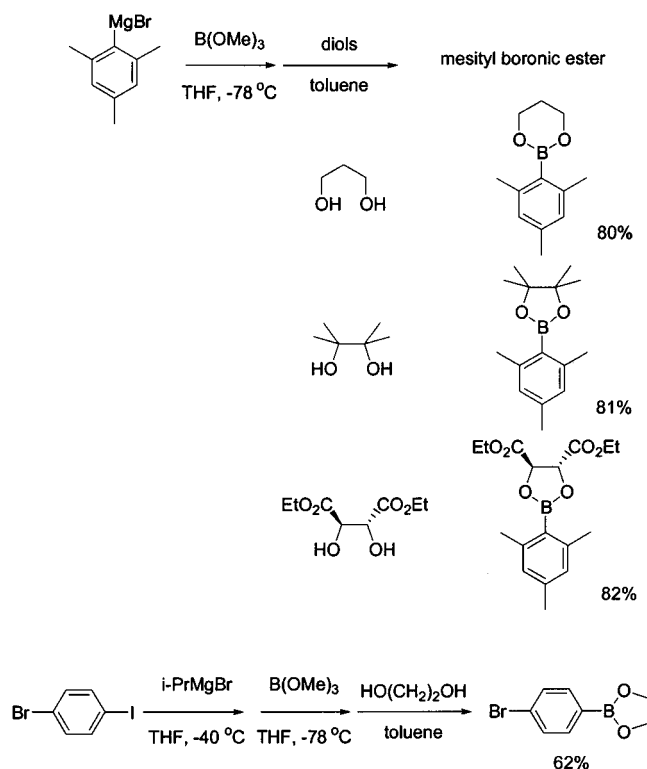
(12) Tse, M. K.; Cho, J.-Y.; Smith, III, M. R. *Org. Lett.* **2001**, *3*, 2831.

Table 1. Isolated Yield of One-Pot Nonaqueous Synthesis of Arylboronic Esters

entry	substrate	product	yield (%)
1			98
2			93
3			85
4			85
5			89
6			80
7			79
8			70
9			65
10			85

Torr to give a yellow white solid. The solid was found to be completely soluble in ethylene glycol, giving a clear solution. The resulting ethylene glycol solution was added with toluene and heated to reflux overnight. The toluene solution was separated and concentrated to afford the corresponding arylboronic ester as a single product.

According to this procedure, a 29 g of phenyl ethylene glycol boronic ester,¹³ which corresponded to a 98% yield, was isolated by reduced pressure distillation. To test the scope and limitation of this protocol, a variety of aryl halides with different structural feature were screened. The isolated yields of arylboronic esters were usually good to excellent (Table 1). 4-Methylphenylboronic ester was isolated in 93% yield as a colorless oil (entry 2). This method was also effective for the synthesis of bulky arylboronic esters. For example, 2,4,6-trimethylphenylboronic ester (mesitylene boronic ester) was isolated with a yield of 85% (entry 3), while steric hindered 1-naphthylboronic ester was isolated in 85% yield (entry 4). It is worthy to note that the 2-biphenylboronic acid¹⁴ was isolated only in 51% yield by a conventional hydrolytic

Scheme 2. One-Pot Synthesis of Arylboronic Esters with Various Diols

workup procedure. By taking advantage of the one-pot, nonaqueous workup procedure, 2-biphenylboronic esters were isolated in 89% yield as a colorless oil (entry 5). The chemoselective Grignard reagent formation at the bromide-substituted aryl carbon in the presence of a *m*-chloro group provides a pathway to synthesize the bifunctional reagent. Accordingly, 3-chlorophenylboronic ester was isolated in 80% yield by using our new procedure (entry 6). The phenyl groups with strong electron-donating substituents were also tested for the efficiency of this new procedure, phenyl groups with a para-substituted diphenylamino group or a methoxy group (entries 7 and 8) give the corresponding boronic esters in lower yields, 79% for 4-OCH₃-phenyl and 70% for 4-Ph₂N-phenyl. Aryldiboronic esters are important building blocks for the synthesis of π -conjugated oligomers and polymers for the optoelectronic uses.¹⁵ According to our new method, the 4,4'-biphenyldiboronic ester was isolated in 65% yield (entry 9). Heteroaryl halides were also suitable for this new method; 2-(5-phenylthienyl) boronic ester was isolated in 85% yield (entry 10).

In addition to using ethylene glycol for this one-pot protocol, 1,3-propanediol, pinacol, and diethyl *L*-tartrate are also applicable for this new procedure to provide the corresponding boronic ester (Scheme 2). The treatment of mesitylenemagnesium bromide with trimethyl borate followed by reaction with 1,3-propanediol gave the boronic ester in 80% yield. 1,3-Propanediol that is insoluble in toluene acts as conveniently as ethylene glycol, providing a well-separated two-phase solution. Thus, the corresponding mesityleneboronic ester can be easily isolated from the toluene solution with comparable yield. How-

(13) Kaminski, J. J.; Lyle, R. E. *Org. Mass Spectrom.* **1978**, *13*, 425.
 (14) Aranyos, A.; Old, D. W.; Kiyomori, A.; Wolfe, J. P.; Sadighi, J. P.; Buchwald, S. L. *J. Am. Chem. Soc.* **1999**, *121*, 4369.

(15) (a) Beley, M.; Chodorowski, S.; Collin, J.-P.; Sauvage, J.-P. *Tetrahedron Lett.* **1993**, *34*, 2933. (b) Yu, W.-L.; Pei, J.; Huang, W.; Heeger, A. J. *Chem. Commun.* **2000**, 681. (c) Yu, W.-L.; Huang, W.; Heeger, A. J. *Adv. Mater.* **2000**, *12*, 828.

ever, when the pinacol and diethyl L-tartrate were used instead of ethylene glycol, the corresponding boronic esters were isolated in 81% and 82% yield, respectively. In these two cases, there are no well-separated two-layer solutions after refluxing overnight due to the partial solubility of pinacol and diethyl L-tartrate in toluene. The isolation of the product was accomplished by directly distilling the resulting mixture under reduced pressure. To widen the scope of this new procedure, the method used to generate the Grignard reagents is not only limited to directly transform from the aryl halides with magnesium metal, but can also be generated by Knochel's exchanging protocol.¹⁶ Accordingly, when 4-iodobromobenzene in THF was treated with ¹PrMgBr (2 equiv) at -40 °C for 3 h, the resulting solution was further reacted with B(OMe)₃ at -78 °C, followed by the new nonaqueous workup procedure giving 4-bromophenylboronic ester in 62% (Scheme 2). The varieties of the methods to generate the Grignard reagents and the different nature of the diols suitable for subsequently workup procedure widely expand the scope of this new procedure.

In summary, we have successfully established an efficient and convenient nonaqueous procedure for the large-scale preparation of arylboronic esters. In one pot, aryl halides that can be transformed into their corresponding Grignard reagents can easily be used for the preparation of aryl boronic ester. The lowest molecular weight diol, ethylene glycol, not only serves as a replacement of water for the workup step but also acts as the reagent for the synthesis of the corresponding boronic esters in good to excellent yields. The boronic residue was dissolved in ethylene glycol, leading to no boron-contaminated aqueous waste. Instead of using ethylene glycol, other diols such as 1,3-propanediol, pinacol, and diethyl L-tartrate are also effective for this new procedure.

Experimental Section

General Experimental Procedure. All reactions were performed under argon and were magnetically stirred. Solvents were distilled from an appropriate drying agent prior to use: THF and Et₂O from sodium and benzophenone, toluene from sodium. Commercially available reagents were used without further purification unless otherwise stated. Melting points were measured on a Fargo MP-1D and are uncorrected. ¹H NMR and ¹³C NMR were recorded using a Bruker (AC-400) or Varian (400 Unity Plus) spectrometer at 400 and 100 MHz, respectively. Low- and high-resolution mass spectra were recorded using a JEOL SX-102A spectrometer in EI mode. Microanalyses were carried out on a Perkin-Elmer 240 analyzer.

Nonaqueous Preparation of Arylboronic Esters. General Procedure. Arylmagnesium halide (1.0 M) prepared from aryl halide (1.0 equiv) and magnesium turnings (1.1 equiv) in THF was added dropwise into a solution of trimethyl borate (2.0 equiv) in THF at -78 °C. The reaction mixture was warmed to room temperature and concentrated to dryness by rotary evaporation distillation (20 Torr). The resulting solid was added ethylene glycol and toluene. The mixture was refluxed overnight, and the toluene layer was separated and concentrated in vacuo to give the corresponding boronic ester.

Representative Procedure for the Nonaqueous Preparation of Arylboronic Esters: 2-Phenyl[1,3,2]dioxaborolane.¹⁷ Phenylmagnesium bromide prepared from bromobenzene (21.0 mL, 200 mmol) and magnesium turning (4.86 g, 200 mmol) in THF (200 mL) was added dropwise into a solution of trimethyl borate (45.7 mL, 400 mmol) in THF (200 mL) at -78 °C. The reaction mixture was warmed to room temperature and concen-

trated to dryness by rotary evaporator distillation (20 Torr). To the resulting solid were added ethylene glycol (30 mL) and toluene (100 mL). The mixture was refluxed overnight, and the toluene layer was separated and concentrated by simple distillation under nitrogen. 2-Phenyl[1,3,2]dioxaborolane (29 g, 98%) was isolated as a colorless oil by distillation under reduced pressure: bp 53–54 °C (0.4 Torr) (lit.¹⁷ bp 57–59 °C); ¹H NMR (CDCl₃, 400 MHz) δ 4.37 (s, 4H), 7.37–7.42 (m, 2H), 7.47–7.49 (m, 1H), 7.83 (d, *J* = 8.0 Hz, 2H); ¹³C NMR (CDCl₃, 400 Hz) δ 66.0, 121.8, 131.4, 134.8.

2-*p*-Tolyl[1,3,2]dioxaborolane.¹⁸ 4-Bromotoluene (3.42 g, 20 mmol), Mg (0.53 g, 22 mmol), trimethyl borate (4.16 g, 40 mmol), THF (20 mL), and ethylene glycol (10 mL), isolated as a white solid (3.01 g, 93%): mp 59–60 °C (lit.¹⁷ mp 60–61 °C); ¹H NMR (CDCl₃, 400 MHz) δ 2.39 (s, 3H), 4.38 (s, 4H), 7.21 (d, *J* = 7.68 Hz, 2H), 7.72 (d, *J* = 7.68 Hz, 1H); ¹³C NMR (CDCl₃, 100 MHz) δ 21.7, 65.9, 128.7, 134.9, 141.7; MS (EI, *m/z*) 162 (70); HRMS (EI) *m/z* calcd for C₉H₁₁BO₂ 162.0859, found 162.0852.

2-(2,4,6-Trimethylphenyl)[1,3,2]dioxaborolane. 1-Bromo-2,4,6-trimethylbenzene (1.0 g, 5.2 mmol), Mg (0.25 g, 10.4 mmol), trimethyl borate (1.08 g, 10.4 mmol), THF (10 mL), ethylene glycol (5 mL), isolated as white solid (0.84 g, 85%): mp 108–109 °C; ¹H NMR (400 MHz, CDCl₃) δ 2.26 (s, 3H), 2.37 (s, 6H), 4.36 (s, 4H), 6.81 (s, 2H); ¹³C NMR (400 MHz, CDCl₃) δ 21.20, 22.49, 65.56, 127.62, 139.35, 142.87; HRMS (FAB) calcd for C₁₁H₁₅BO₂ 190.1163, found 190.1165. Anal. Calcd for C₁₁H₁₅BO₂: C, 69.52; H, 7.96. Found: C, 69.44; H, 8.20.

2-(1-Naphthyl)[1,3,2]dioxaborolane.¹⁹ 1-Bromonaphthalene (2.07 g, 10.0 mmol), Mg (0.27 g, 11.0 mmol), trimethyl borate (2.08 g, 20.0 mmol), THF (10 mL), ethylene glycol (5 mL), isolated as a white solid (1.68 g, 85%): mp 57–58 °C (lit.¹⁹ mp 146–149 °C); ¹H NMR (CDCl₃, 400 MHz) δ 4.49 (s, 4H), 7.48–7.55 (m, 3H), 7.86 (d, *J* = 8.8 Hz, 1H), 7.97 (d, *J* = 8.2 Hz, 1H), 8.13 (d, *J* = 5.8 Hz, 1H), 8.76 (d, *J* = 8.9 Hz, 1H); ¹³C NMR (CDCl₃, 100 MHz) δ 65.9, 125.0, 125.6, 126.5, 128.3, 128.4, 132.0, 133.2, 136.1, 136.9; MS (EI, *m/z*) 198 (100); HRMS (EI) calcd for C₁₂H₁₁BO₂ 198.0852, found 198.0865.

2-(2-Biphenyl)[1,3,2]dioxaborolane. 2-Bromobiphenyl (2.79 g, 10.0 mmol), Mg (0.26 g, 11.0 mmol), trimethyl borate (2.08 g, 20.0 mmol), diethyl ether (10 mL), ethylene glycol (5 mL), isolated as a colorless oil (2.01 g, 89%): ¹H NMR (CDCl₃, 400 MHz) δ 4.22 (s, 4H), 7.35–7.42 (m, 7H), 7.50 (td, *J* = 7.43, 1.4 Hz, 3H), 7.83 (dd, *J* = 7.37, 1.0 Hz, 1H); ¹³C NMR (acetone-*d*₆, 100 MHz) δ 66.0, 126.9, 127.2, 127.5, 127.9, 128.4, 129.0, 219.4, 129.5, 131.0, 135.2, 140.7, 147.6; MS (EI, *m/z*) 224 (100); HRMS (EI) calcd for C₉H₁₁BO₃ 178.0801, found 178.0809.

2-(3-Chlorophenyl)[1,3,2]dioxaborolane. 3-Chlorobromobenzene (3.83 g, 20.0 mmol), Mg (0.53 g, 22.0 mmol), trimethyl borate (4.16 g, 40.0 mmol), THF (20 mL), ethylene glycol (10 mL), isolated as a colorless oil (2.92 g, 80%): bp 68–70 °C (0.5 Torr); ¹H NMR (CDCl₃, 400 MHz) δ 4.39 (s, 4H), 7.31 (t, *J* = 7.7 Hz, 1H), 7.44 (d, *J* = 8.0 Hz, 1H), 7.67 (d, *J* = 7.3 Hz, 1H), 7.78 (s, 1H); ¹³C NMR (CDCl₃, 100 MHz) δ 66.2, 129.3, 131.5, 132.7, 134.1, 134.7; MS (EI, *m/z*) 182 (43), 184 (14); HRMS (EI) calcd for C₈H₈B³⁵ClO₂ 182.0306, found 182.0310; calcd for C₈H₈B³⁷ClO₂ 184.0276, found 184.0268.

2-(4-Methoxyphenyl)[1,3,2]dioxaborolane.²⁰ 4-Bromoanisole (3.74 g, 20 mmol), Mg (0.53 g, 22 mmol), trimethyl borate (4.16 g, 40 mmol), THF (20 mL), ethylene glycol (10 mL), isolated as a light yellow solid (2.80 g, 79%): mp 36–37 °C (lit.¹⁷ mp 50–52 °C); ¹H NMR (CDCl₃, 400 MHz) δ 3.84 (s, 3H), 4.36 (s, 4H), 6.92 (d, *J* = 8.3 Hz, 3H), 7.77 (d, *J* = 8.3 Hz, 1H); ¹³C NMR (CDCl₃, 100 MHz) δ 55.1, 65.9, 113.5, 136.6, 162.3; MS (EI, *m/z*) 178 (100); HRMS (EI) calcd for C₉H₁₁BO₃ 178.0801, found 178.0809.

2-(4-Diphenylaminophenyl)[1,3,2]dioxaborolane. (4-Bromophenyl)diphenylamine²¹ (1.0 g, 3.1 mmol), Mg (0.15 g, 6.2 mmol), trimethyl borate (0.65 g, 6.2 mmol), THF (10 mL), ethylene glycol (1.6 mL), isolated as a waxy solid (0.68 g, 70%): ¹H NMR (CDCl₃, 400 MHz) δ 4.36 (s, 4H), 7.15–7.03 (m, 8H), 7.30–7.26 (m, 4H), 7.67 (d, *J* = 8.6 Hz, 2H); ¹³C NMR (CDCl₃,

(18) Longstaff, C.; Rose, M. E. *Org. Mass Spectrom.* **1982**, *17*, 508.

(19) Ingham, R. K.; Huntsman, W. D. *Chem. Abstr.* **1963**, *58*, 4587e.

(20) Wallow, T. I.; Novak, B. M. *J. Org. Chem.* **1994**, *59*, 9; 17.

(21) Creson, S. C.; Wheeler, J.; Nelson, R. F. *J. Org. Chem.* **1972**, *37*, 4440.

(16) Boymond, L.; Rottlander, M.; Gahiez, G.; Knochel, P. *Angew. Chem., Int. Ed. Engl.* **1998**, *37*, 1701.

(17) Kaminski, J. J.; Lyle, R. E. *Org. Mass Spectrom.* **1978**, *13*, 425.

100 MHz) δ 65.96, 121.43, 123.56, 125.22, 129.35, 135.93, 147.29; MS (EI, *m/z*) 315 (100); HRMS (FAB) calcd for C₂₀H₁₈BNO₂ 315.1431, found 315.1427.

Biphenyl-4,4'-ethylene Glycol Diboronic Ester.²² 4,4'-Dibromobiphenyl (3.12 g, 10.0 mmol), Mg (0.53 g, 22.0 mmol), trimethyl borate (4.16 g, 40.0 mmol), THF (20 mL), ethylene glycol (5 mL), isolated as a pale yellow solid (1.91 g, 65%): mp 288–289 °C; ¹H NMR (CDCl₃, 400 MHz) δ 4.41 (s, 8H), 7.66 (d, *J* = 4.9 Hz, 4H), 7.90 (d, *J* = 4.9 Hz, 4H); ¹³C NMR (CDCl₃, 100 MHz) δ 66.0, 126.6, 135.3, 143.7; MS (EI, *m/z*) 294(100); HRMS (EI) calcd for C₁₆H₁₆B₂O₄ 294.1235, found 294.1240.

2-(5-Phenylthienyl)ethylene Glycol Boronic Ester. 2-Bromo-5-phenylthiophene²³ (1.2 g, 5.0 mmol), Mg (0.132 g, 5.5 mmol), trimethyl borate (1.04 g, 10.0 mmol), THF (10 mL), ethylene glycol (3 mL), isolated as a white solid (0.98 g, 85%): mp 111–112 °C; ¹H NMR (CDCl₃, 400 MHz) δ 4.40 (s, 4H), 7.26–7.33 (m, 1H), 7.38–7.42 (m, 3H), 7.66 (d, *J* = 3.6 Hz, 1H), 7.67 (d, *J* = 6.0 Hz, 2H); ¹³C NMR (CDCl₃, 100 MHz) δ 66.1, 124.5, 126.2, 128.0, 128.9, 134.0, 138.5, 151.7; MS (EI, *m/z*) 230 (100); HRMS (EI) calcd for C₁₂H₁₁BO₂S 230.0573, found 230.0565.

2-(2,4,6-Trimethylphenyl)[1,3,2]dioxaborinane. 1-Bromo-2,4,6-trimethylbenzene (3.98 g, 20.0 mmol), Mg (0.53 g, 22 mmol), trimethyl borate (4.16 g, 40 mmol), THF (20 mL), 1,3-propanediol (5 mL), isolated as a white solid (3.2 g, 80%): mp 48–49 °C; ¹H NMR (CDCl₃, 400 MHz) δ 2.10 (qn, *J* = 5.5 Hz, 2H), 2.24 (s, 3H), 2.33 (s, 6H), 4.17 (t, *J* = 5.5 Hz, 4H), 6.77 (s, 2H); ¹³C NMR (CDCl₃, 100 MHz) δ 21.2, 21.9, 27.7, 62.0, 127.1, 137.9, 140.3; MS (EI, *m/z*) 204 (100); HRMS (EI *m/z*) calcd for C₁₂H₁₇BO₂ 204.1322, found 204.1322.

Mesitylpinacol Boronate Ester. 2-Bromo-2,4,6-trimethylbenzene (3.98 g, 20.0 mmol), Mg (0.53 g, 22 mmol), trimethyl borate (4.16 g, 40 mmol), THF (20 mL), pinacol (7.08 g), isolated as a colorless oil (4.0 g, 81%): bp 125 °C bulb-to-bulb (0.1 Torr); ¹H NMR (CDCl₃, 400 MHz) δ 1.38 (s, 12H), 2.25 (s, 3H), 2.38 (s,

6H), 6.78 (s, 2H); ¹³C NMR (CDCl₃, 100 MHz) δ 21.2, 22.2, 24.9, 83.4, 127.4, 138.9, 142.1; MS (EI, *m/z*) 246 (100); HRMS (EI *m/z*) calcd for C₁₅H₂₃BO₂ 246.1791, found 246.1794.

Mesityl Diethyl L-Tartrate Boronate Ester. 2-Bromo-2,4,6-trimethylbenzene (3.98 g, 20.0 mmol), Mg (0.53 g, 22 mmol), trimethyl borate (4.16 g, 40 mmol), THF (20 mL), diethyl L-tartrate (10 mL), isolated as a colorless oil (5.47 g, 82%): ¹H NMR (CDCl₃) δ 1.35 (t, *J* = 2.76 Hz, 6H), 2.29 (s, 3H), 2.47 (s, 6H), 4.34 (q, *J* = 2.76 Hz, 4H), 5.04 (s, 2H), 6.85 (s, 2H); ¹³C NMR (CDCl₃, 100 MHz) δ 14.1, 21.3, 22.4, 62.2, 127.8, 169.7, 140.2, 143.7; MS (EI, *m/z*) 334 (100); HRMS (EI *m/z*) calcd for C₁₇H₂₃BO₆ 334.1588, found 334.1580.

2-(4-Bromophenyl)[1,3,2]dioxaborolane.¹⁷ 2-Propylmagnesium bromide prepared from 2-bromopropane (0.94 mL, 10 mmol) and Mg (0.243 g, 10 mmol) in THF (10 mL) was added dropwise into a solution of 4-iodobromobenzene (1.41 g, 5.0 mmol) in THF (10 mL) at –40 °C. The mixture was stirred for 3 h and cooled to –78 °C. Trimethyl borate (1.15 mL, 10 mmol) was added in one portion at –78 °C. After the mixture was warmed to room temperature and following the general workup procedure, the desired product was isolated as a white solid (0.7 g, 62%): mp 96–97 °C (lit.¹⁷ mp 97–99 °C); ¹H NMR (CDCl₃, 400 MHz) δ 4.37 (s, 4H), 7.54 (d, *J* = 8.31 Hz, 2H), 7.67 (d, *J* = 8.31 Hz, 2H); ¹³C NMR (CDCl₃, 100 MHz) δ 66.1, 126.5, 131.1, 136.3; MS (EI, *m/z*) 225 (100); HRMS (EI) calcd for C₈H₈B⁸¹BrO₂ 225.9801, found 225.9799; Calcd for C₈H₈B⁸¹BrO₂ 227.9780, found 227.9784.

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Supporting Information Available: ¹H and ¹³C NMR spectra (PDF) for all arylboronic esters. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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(22) Beley, M.; Chodorowski, S.; Collin, J.-P.; Sauvage, J.-P. *Tetrahedron Lett.* **1993**, *34*, 2933.

(23) Hotta, S.; Lee, S. A.; Tamaki, T. *J. Heterocycl. Chem.* **2000**, *37*, 25.