Tetrahedron Letters 54 (2013) 166–169

Contents lists available at SciVerse ScienceDirect

Tetrahedron Letters

journal homepage: www.elsevier.com/locate/tetlet

Syntheses of (4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)arenes through Pd-catalyzed borylation of arylbromides with the successive use of 2,2′-bis(1,3,2-benzodioxaborole) and pinacol

Jun Takagi, Tetsu Yamakawa *

Sagami Chemical Research Institute, Catalysis Group, Hayakawa 2743-1, Ayase, Kanagawa 252-1193, Japan

ARTICLE INFO

Article history:
Received 18 September 2012
Revised 24 October 2012
Accepted 29 October 2012
Available online 3 November 2012

Keywords:
(4,4,5,5-Tetramethyl-1,3,2-dioxaborolan-2-yl)arenes
2,2′-Bis(1,3,2-benzodioxaborole)
Pd catalyst
Borylation

ABSTRACT

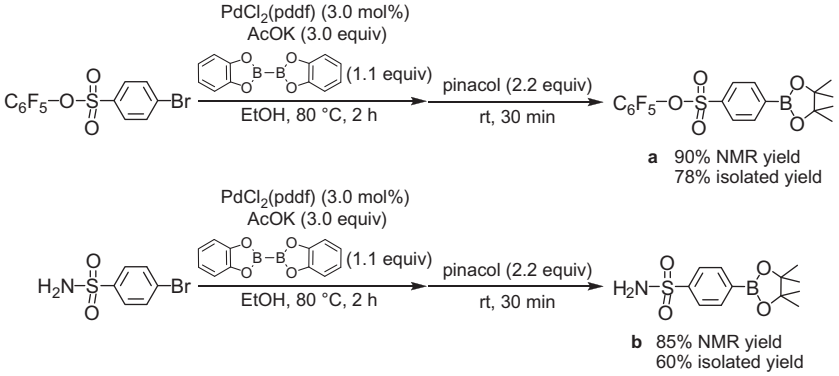
Syntheses of (4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)arenes through the Pd-catalyzed borylation of arylbromides with the successive use of 2,2′-bis(1,3,2-benzodioxaborole) and pinacol were investigated. $PdCl_2$(dppf) and AcOK in EtOH or DMSO successfully provided (4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)arenes. In particular, this method was more effective in the borylation of arylbromides bearing sulfonyl groups than the conventional Pd-catalyzed borylation using pinacolborane or bis(pinacolato)diboron.

Arylboronic acids and their diol-esters are important reagents in organic synthesis[1] and the applications in transition metal-catalyzed C–C, C–N, and C–O bond formations render them as some of the most useful synthetic reagents in both academic laboratories and industry.[2] Particularly, (4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)arenes (pinB-Ar) are some of the most available reagents because of their stability against air and moisture.[1] Numerous number of reports have been published regarding the syntheses of pinB-Ar through transition-metal catalyzed borylation of arenes[3] or arylhalides[4] with pinacolborane (pinBH) or bis(pinacolato)diboron (pin_2B_2). Although these borylations are widely applicable to a variety of substrates, they are unsatisfactory for pinB-Ar syntheses from substrates bearing several specific substituents. Sulfonyl groups are instances of such substituents. On the other hand, some sulfonated pinB-Ar are important intermediates in the synthesis of medicines. For example, pentafluorophenyl 4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)benzenesulfonate (**a**) is an intermediate in the synthesis of protein kinase inhibitors[5] and IKK2 inhibitors,[6] and 4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)benzenesulfonamide (**b**) is an intermediate in the synthesis of phosphodiesterase inhibitors.[7] The reported synthetic methods of compounds **a** and **b** employed conventional Pd-catalyzed borylations using pinBH or pin_2B_2. Compound **a** was synthesized from pentafluorophenyl 4-bromobenzenesulfonate and pin_2B_2[5] or pinBH[6] in the presence of $PdCl_2$(dppf) (3.0 mol %), dppf (3.0 mol %), and AcONa in 1,4-dioxane at 105 °C for 16 h. This conventional borylation afforded rather low yields, 37% and 14%, respectively. Compound **b** was obtained from 4-bromobenzenesulfonamide and pin_2B_2 in a moderate yield (68%) by the use of $PdCl_2$(dppf) (2.7 mol %) and AcOK in DMSO at 80 °C.[7] Nevertheless, a somewhat long reaction time, 16 h, was required.

In the search for an efficient process for the borylation of these sulfonated arylbromides, we found that the successive use of 2,2′-bis(1,3,2-benzodioxaborole) (cat_2B_2) and pinacol with $PdCl_2$(dppf) catalyst successfully provided moderate yields. Thus, after heating a mixture of cat_2B_2, $PdCl_2$(dppf), pentafluorophenyl 4-bromobenzenesulfonate, and AcOK in EtOH at 80 °C for 2 h, followed by the addition of pinacol and stirring at room temperature for 30 min, **a** was obtained in 90% ^{1}H NMR yield. The product was isolated as a white solid in 78% yield (Scheme 1).[8,9] In addition, the borylation of 4-bromobenzenesulfonamide under the same conditions provided **b** in 85% ^{1}H NMR yield and 60% isolated yield. The yield of **a** was obviously superior to the literature data.[5,6] While the yield of **b** was slightly lower than the reported yield,[7] the reaction time was considerably shorter than that for the reported borylation using pin_2B_2. Although cat_2B_2 is an expensive reagent, we can present the advantage of the present borylation in the syntheses of sulfonated pinB-Ar. Interestingly, both reactions afforded low yields in DMSO solvent, which is generally used in conventional borylation: 0% and 45% ^{1}H NMR yields, respectively.

* Corresponding author. Tel.: +81 467769268; fax: +81 467774113.
E-mail address: t_yamakawa@sagami.or.jp (T. Yamakawa).

0040-4039/$ - see front matter © 2012 Elsevier Ltd. All rights reserved.
http://dx.doi.org/10.1016/j.tetlet.2012.10.118



Scheme 1. Pd-catalyzed borylation of pentafluorophenyl 4-bromobenzenesulfonate and 4-bromobenzenesulfonamide with the successive use of cat_2B_2 and pinacol.

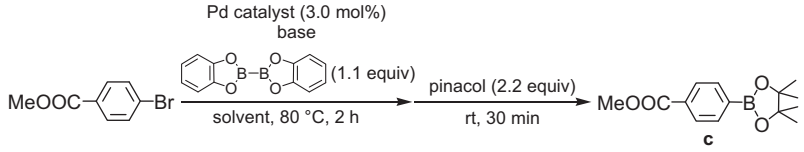
Then, we examined the application of this borylation to the other substrates. At first, the reaction conditions were surveyed using methyl 4-bromobenzoate as the substrate. Representative results for the synthesis of methyl 4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)benzoate (**c**) are listed in Table 1.[8,9]

$PdCl_2$(dppf) quantitatively provided **c** (entry 1). The combined use of $PdCl_2(MeCN)_2$ or $Pd(OAc)_2$ and PPh_3 afforded moderate yields (entries 2 and 3). The use of AcONa also produced an excellent yield (entry 4). Alcohols other than EtOH were suitable as a solvent for this reaction except ^{t}BuOH (entries 5–9). As in the case of the reactions in Scheme 1, the yield was drastically reduced by the use of DMSO (entry 10). This low yield was improved to excellent yields by increasing the amount of AcOK to 7.2 mmol (entry 11). Borylation using 7.2 mmol of AcOK also gave an excellent yield even with ^{t}BuOH as a solvent (entry 12). Various Pd catalysts or substituted cat_2B_2 provided excellent yields with 7.2 mmol of AcOK in DMSO (entries 13–17). In contrast to the borylation in entry 4, the yield was declined with 7.2 mmol of AcONa instead of AcOK (entry 18).

Next, the scope and limitations of the substrates were investigated. Based on the results in Table 1, we performed the borylation under two conditions: 3.0 mmol of AcOK in EtOH (conditions **A**) and 7.2 mmol of AcOK in DMSO (conditions **B**). We chose the higher yield from the results obtained under these two conditions for each substrate and summarized them in Table 2.[8,9] A variety of functional groups did not retard the reaction except in the case of entries 3, 5, 8, 12, and 14. In the first three of these substrates, the functional groups which exist at the *ortho*-position to bromine presumably result in a sterically unfavorable environment.

To date, two similar pinB-Ar syntheses by the use of catecholborane derivatives were reported.[10] One is the Pd-catalyzed synthesis of 2-(1-naphthyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane through the reaction of 1-iodonaphthalene and catecholborane (catBH) followed by the addition on pinacol.[10a] Another is 2-aryl-4,4,5,5-tetramethyl-1,3,2-dioxaborolanes syntheses from arylbromides and 2-chloro- or 2-bromo-1,3,2-benzodioxaborole (catB-Cl or catB-Br) in the presence of $CoBr_2$ and Zn followed by the addition of pinacol.[10b] In both cases, a catB-Ar is considered to be an

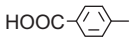
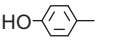
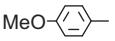
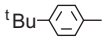
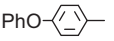
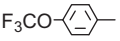
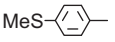
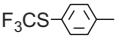
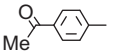
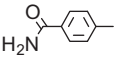
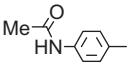
Table 1
Pd-catalyzed borylation of 4-bromobenzoate with the successive use of cat_2B_2 and pinacol under various conditions[a]



Entry	Pd catalyst	Base	Solvent	Yield[b] (%)
1	$PdCl_2$(dppf)	AcOK (3.0 mmol)	EtOH	99 (96)
2	$PdCl_2(MeCN)_2 + (PPh_3)$	AcOK (3.0 mmol)	EtOH	83
3	$Pd(AcO)_2 + PPh_3$	AcOK (3.0 mmol)	EtOH	71
4	$PdCl_2$(dppf)	AcONa (3.0 mmol)	EtOH	98
5	$PdCl_2$(dppf)	AcOK (3.0 mmol)	PrOH	99
6	$PdCl_2$(dppf)	AcOK (3.0 mmol)	^{i}PrOH	99
7	$PdCl_2$(dppf)	AcOK (3.0 mmol)	^{t}BuOH	46
8	$PdCl_2$(dppf)	AcOK (3.0 mmol)	*n*-Hexanol	99
9	$PdCl_2$(dppf)	AcOK (3.0 mmol)	Cyclohexanol	86
10	$PdCl_2$(dppf)	AcOK (3.0 mmol)	DMSO	56
11	$PdCl_2$(dppf)	AcOK (7.2 mmol)	DMSO	99 (96)
12	$PdCl_2$(dppf)	AcOK (7.2 mmol)	^{t}BuOH	94
13	$PdCl_2(PPh_3)_2$	AcOK (7.2 mmol)	DMSO	99
14	$Pd(PPh_3)_4$	AcOK (7.2 mmol)	DMSO	97
15	$PdCl_2 + 2PPh_3$	AcOK (7.2 mmol)	DMSO	99
16	$PdCl_2(MeCN)_2 + (PPh_3)$	AcOK (7.2 mmol)	DMSO	96
17[c]	$PdCl_2$(dppf)	AcOK (7.2 mmol)	DMSO	90
18	$PdCl_2$(dppf)	AcONa (7.2 mmol)	DMSO	52

[a] Methyl 4-bromobenzoate 1.0 mmol, solvent 6.0 mL.
[b] ^{1}H NMR yield. Isolated yields are shown in parentheses.
[c] 5,5′-Di-*tert*-butyl-2,2′-bis(1,3,2-benzodioxaborole) was used instead of cat_2B_2.

Table 2
Scope and limitations of substrates in Pd-catalyzed borylation with the successive use of cat_2B_2 and pinacol[a]

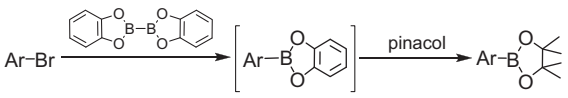
Entry	Ar	Conditions	Isolated yield (%)	Entry	Ar	Conditions	Isolated yield (%)
1		A	60 (**d**)	11		A	84 (**n**)
2		B	72 (**e**)	12		A	44 (**o**)
3		B	48 (**f**)	13		A	95 (**p**)
4		B	88 (**g**)	14		B	49 (**q**)
5		B	44 (**h**)	15		B	78 (**r**)
6		A	92 (**i**)	16		B	97 (**s**)
7		A	82 (**j**)	17		B	99 (**t**)
8		B	56 (**k**)	18		A	85 (**u**)
9		A	63 (**l**)	19		A	77 (**v**)
10		A	99 (**m**)	20		B	72 (**w**)
				21		A	65 (**x**)

[a] All the products are known compounds and were isolated as a white solid see Ref. 9.

intermediate, though it was not isolated. It seems likely that a catB-Ar is highly sensitive to moisture and chromatogram and favors transesterification with pinacol. We also could not isolate a catB-Ar from the reaction mixture in the present borylation. Nevertheless, a catB-Ar that can be formed through the Pd-catalyzed borylation of arylbromides with cat_2B_2 is probably an intermediate (Scheme 2).

As described above, the present borylation is advantageous in the synthesis of sulfonated pinB-Ar. On the other hand, recent interests in borylation are focused in the large-scale synthesis of pinB-Ar using convenient reagents. For example, Molandar and co-workers reported the borylation of arylchlorides with $B_2(OH)_4$ in the presence of Pd/X-Phos catalyst.[11] $ArB(OH)_2$ thus generated in the reaction mixture was readily esterificated with pinacol to pinB-Ar in a one-pot reaction. Schmidt-Leithoff and co-worker reported Pd-catalyzed borylation of arylhalides or triflates with pin_2B_2 that was generated in situ through the esterification of $(Me_2N)_2B–B(NMe_2)_2$ with pinacol.[12] Since both $B_2(OH)_4$ and $(Me_2N)_2B–B(NMe_2)_2$ are stable and easy to handle, these processes should be suitable for the large-scale synthesis of pinB-Ar. Cat_2B_2 is also a stable reagent which is solid at room temperature. From that point of view, our method seems advantageous for large-scale synthesis of pinB-Ar.

In conclusion, we presented a new route for the synthesis of pinB-Ar from arylbromides in the presence of a Pd catalyst. This method characteristically exhibited a high yield with sulfonated arylbromides which previously afforded rather low yields via conventional borylation using pinBH or pin_2B_2. Mechanistic considerations and the application to a one-pot Suzuki–Miyaura coupling are now under investigation.



Scheme 2. Speculated reaction scheme of Pd-catalyzed borylation with the successive use of cat_2B_2 and pinacol.

References and notes

1. *Boronic Acids*; Hall, D. G., Ed.; Wiley-VCH: Weinheim, 2005.
2. Recent reviews: (a) Liu, C.; Zhang, H.; Shi, W.; Lei, A. *Chem. Rev.* **2011**, *111*, 1780–1824; (b) Partyka, D. V. *Chem. Rev.* **2011**, *111*, 1529–1595; (c) Rosen, B. M.; Quasdorf, K. W.; Wilson, D. A.; Zhang, N.; Resmerita, A. M.; Garg, N. K.; Percec, V. *Chem. Rev.* **2011**, *111*, 1346–1416.
3. Recent papers and reviews: (a) Xiao, B.; Li, Y.-M.; Liu, Z.-J.; Yang, H.-Y.; Fu, Y. *Chem. Commun.* **2012**, *48*, 4854–4856; (b) Roering, A. J.; Hale, L. V. A.; Squier, P. A.; Ringgold, M. A.; Wiederspan, E. R.; Clark, T. B. *Org. Lett.* **2012**, *14*, 3558–3561; (c) Hartwig, J. F. *Chem. Soc. Rev.* **2011**, *40*, 1992–2002; (d) Yamazaki, K.; Kawamorita, S.; Ohmiya, H.; Sawamura, M. *Org. Lett.* **2010**, *12*, 3978–3981; (e) Mkhalid, I. A. I.; Barnard, J. H.; Marder, T. B.; Murphy, J. M.; Hartwig, J. F. *Chem. Rev.* **2010**, *110*, 890–931; (f) Robbins, D. W.; Boebel, T. A.; Hartwig, J. F. *J. Am. Chem. Soc.* **2010**, *132*, 4068–4069; (g) Kawamorita, S.; Ohmiya, H.; Sawamura, M. *J. Org. Chem.* **2010**, *75*, 3855–3858; (h) Ishiyama, T.; Isou, H.; Kikuchi, T.; Miyaura, N. *Chem. Commun.* **2010**, *46*, 159–161; (i) Boebel, T. A.; Hartwig, J. F. *J. Am. Chem. Soc.* **2008**, *130*, 7534–7535; (j) Miyaura, N. *Bull. Chem. Soc. Jpn.* **2008**, *81*, 1535–1553; (k) Ishiyama, T.; Murata, M.; Miyaura, N. *J. Org. Chem.* **1995**, *60*, 7508–7510.
4. Recent papers: (a) Yamamoto, T.; Morita, T.; Takagi, J.; Yamakawa, T. *Org. Lett.* **2011**, *13*, 5766–5769; (b) Tang, M.; Keshipeddy, S.; Zhang, Y.; Wei, X.; Savoie, J.; Patel, N. D.; Yee, N. K.; Senanayake, C. H. *Org. Lett.* **2011**, *13*, 1366–1369; (c) Kawamorita, S.; Ohmiya, H.; Iwai, T.; Sawamura, M. *Angew. Chem., Int. Ed.* **2011**, *50*, 8363–8366; (d) Murata, M.; Sambommatsu, T.; Oda, T.; Watanabe, S.; Masuda, Y. *Heterocycles* **2010**, *80*, 213–218; (e) Kleeberg, C.; Dang, L.; Lin, Z. Y.; Marder, T. B. *Angew. Chem., Int. Ed.* **2009**, *48*, 5350–5354; (f) Billingsley, K. L.; Buchwald, S. L. *J. Org. Chem.* **2008**, *73*, 5589–5591; (g) Bilingsley, K. L.; Barder, T. E.; Buchwald, S. L. *Angew. Chem., Int. Ed.* **2007**, *46*, 5359–5363.
5. Hamajima, T.; Nakamura, H.; Tang, J. WO2007-076320.
6. Bamborough, P.; Marker, M. D.; Camps, S. A.; Cousins, R. P. C.; Faulhobbs, H.; Holmes, D. S.; Johnston, M. J.; Liddle, J.; Payne, J. J.; Pritchard, J. M.; Whitworth, C. WO2008-034860.

7. Bollbuck, B.; Denholm, A.; Eder, J.; Hersperger, R.; Janser, P.; Révész, L.; Schlapbach, A. Wälchli, R. WO2004-089913.
8. *General procedure*: The synthetic procedure for pentafluorophenyl 4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolane-2-yl)benzenesulfonate (a) is presented as an example (Scheme 1). 2,2′-Bis(1,3,2-benzodioxaborole) (cat2B2, 262 mg, 1.10 mmol), PdCl2(dppf) (25 mg, 0.030 mmol), AcOK (294 mg, 3.0 mmol), pentafluorophenyl 4-bromobenzenesulfonate (403 mg, 1.0 mmol), and EtOH (6.0 mL) were charged in a reaction vessel under an Ar atmosphere. The resulting mixture was stirred for 2 h at 80 °C. After cooling to room temperature, pinacol (260 mg, 2.20 mmol) was added to the mixture. The mixture was further stirred for 30 min at room temperature. H_2O and *n*-hexane were added to the mixture and the product was extracted into the organic layer. After drying the organic layer with anhydrous $MgSO_4$, solids were removed by filtration. The filtrate was concentrated. The product was obtained as a white solid by Kugelrohr distillation.
9. *Characterization of products*: All the products were given CAS numbers. We characterized each compound by ^{1}H NMR. The chemical shifts (δ, ppm to $SiMe_4$) in $CDCl_3$ were listed below. Pentafluorophenyl 4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)benzenesulfonate (**a**, 928656-94-4): 1.32 (12H, s), 7.95 (2H, d, *J* = 8.6 Hz), 8.02 (2H, d, *J* = 8.6 Hz). 4-(4,4,5,5-Tetramethyl-1,3,2-dioxaborolan-2-yl)benzenesulfonamide (**b**, 214360-51-7): 1.36 (12H, s), 4.75 (2H, s), 7.91 (2H, d, *J* = 8.4 Hz), 7.95 (2H, d, *J* = 8.4 Hz). Methyl 4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)benzoate (**c**, 171364-80-0): 1.36 (12H, s), 3.92 (3H, s), 7.87 (2H, d, *J* = 8.4 Hz), 8.02 (2H, d, *J* = 8.4 Hz). 4-(4,4,5,5-Tetramethyl-1,3,2-dioxaborolan-2-yl)benzoic acid (**d**, 180516-87-4): 1.36 (12H, s), 7.90 (2H, d, *J* = 8.3 Hz), 8.08 (2H, d, *J* = 8.3 Hz). 2-(3,5-Dimethylphenyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (**e**, 325142-93-6): 1.34 (12H, s), 2.32 (6H, s), 7.10 (1H, s), 7.44 (2H, s). 2-(2,6-Dimethylphenyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (**f**, 325141-72-8): 1.38 (12H, s), 2.39 (6H, s), 6.94 (1H, s, *J* = 7.3 Hz), 7.12 (1H, s, *J* = 7.3 Hz). 2-(4-*tert*-Butylphenyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (**g**, 214360-66-4): 1.32 (9H, s), 1.33 (12H, s), 7.40 (2H, d, *J* = 8.3 Hz), 7.75 (2H, d, *J* = 8.3 Hz). 2-(4,4,5,5-Tetramethyl-1,3,2-dioxaborolan-2-yl)benzotrifluoride (**h**, 1073339-21-5): 1.37 (12H, s), 7.49–7.51 (2H, m), 7.65–7.67 (1H, m), 7.71–7.73 (1H, m). 2-[3,5-Bis(trifluoromethyl)phenyl]-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (**i**, 69807-91-6): 1.37 (12H, s), 7.94 (1H, s), 8.23 (2H, s). 2-(4-Chlorophenyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (**j**, 195062-61-4): 1.34 (12H, s), 7.34 (2H, d, *J* = 8.4 Hz), 7.73 (2H, d, *J* = 8.4 Hz). 2-(2-Chlorophenyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (**k**, 870195-94-1): 1.37 (12H, s), 7.20–7.24 (1H, m), 7.33–7.34 (2H, m), 7.68 (1H, d, *J* = 7.4 Hz). 2-(3,4-Difluorophenyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (**l**, 754226-39-6): 1.33 (12H, s), 7.14 (1H, d, *J* = 10.7 Hz), 7.50–7.54 (1H, m), 7.56–7.60 (1H, m). 2-(3,4,5-Trifluorophenyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (**m**, 827614-70-0): 1.33 (12H, s), 7.36–7.40 (2H, m). 4-(4,4,5,5-Tetramethyl-1,3,2-dioxaborolan-2-yl)benzonitrile (**n**, 171364-82-2): 1.35 (12H, s), 7.64 (2H, d, *J* = 8.4 Hz), 7.88 (2H, d, *J* = 8.4 Hz). 4-(4,4,5,5-Tetramethyl-1,3,2-dioxaborolan-2-yl)phenol (**o**, 269409-70-3): 1.33 (12H, s), 4.79 (1H, s), 6.82 (2H, d, *J* = 8.6 Hz), 7.71 (2H, d, *J* = 8.6 Hz). 2-(4-Methoxyphenyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (**p**, 171364-79-7): 1.33 (12H, s), 3.83 (3H, s), 6.89 (2H, d, *J* = 8.7 Hz), 7.75 (2H, d, *J* = 8.7 Hz). Phenyl[4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)]phenyl ether (**q**, 269410-26-6): 1.34 (12H, s), 6.98 (2H, d, *J* = 8.6 Hz), 7.01–7.03 (2H, m), 7.13 (1H, tt, *J* = 1.0, 7.4 Hz), 7.32–7.37 (2H, m), 7.78 (2H, d, *J* = 8.6 Hz). 2-[4-(Trifluoromethoxy)phenyl]-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (**r**, 474409-28-9): 1.34 (12H, s), 7.20 (2H, d, *J* = 8.8 Hz), 7.84 (2H, d, *J* = 8.8 Hz). 5-(4,4,5,5-Tetramethyl-1,3,2-dioxaborolan-2-yl)-1,3-benzodioxole (**s**, 94838-82-1): 1.32 (12H, s), 5.95 (2H, s), 6.83 (1H, d, *J* = 7.9 Hz), 7.24 (1H, s), 7.36 (1H, dd, *J* = 1.1, 7.9 Hz). 2-(4-Methylthiophenyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (**t**, 190788-58-0): 1.33 (12H, s), 2.49 (3H, s), 7.22 (2H, d, *J* = 8.3 Hz), 7.70 (2H, d, *J* = 8.3 Hz). 2-[4-(Trifluoromethylthio)phenyl]-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (**u**, 1005206-25-6): 1.35 (12H, s), 7.64 (2H, d, *J* = 8.3 Hz), 7.84 (2H, d, *J* = 8.3 Hz). 1-[4-(4,4,5,5-Tetramethyl-1,3,2-dioxaborolane-2-yl)phenyl]ethanone (**v**, 171364-81-1): 1.36 (12H, s), 2.62 (3H, s), 7.89 (2H, d, *J* = 8.4 Hz), 7.93 (2H, d, *J* = 8.4 Hz). 4-(4,4,5,5-Tetramethyl-1,3,2-dioxaborolan-2-yl)benzamide (**w**, 179117-44-3): 1.35 (12H, s), 7.80 (2H, d, *J* = 7.3 Hz), 7.88 (2H, d, *J* = 7.3 Hz). 4-(4,4,5,5-Tetramethyl-1,3,2-dioxaborolan-2-yl)acetanilide (**x**, 214360-60-8): 1.34 (12H, s), 2.18 (3H, s), 7.51 (2H, d, *J* = 8.3 Hz), 7.76 (2H, d, *J* = 8.3 Hz).
10. (a) Murata, M.; Oyama, T.; Watanabe, S.; Masuda, Y. *J. Org. Chem.* **2000**, *65*, 164–168; (b) Claudel, S.; Gosmini, C.; Paris, J. M.; Périchon, J. *Chem. Commun.* **2007**, 3667–3669.
11. Molander, G. A.; Trice, S. L. J.; Dreher, S. D. *J. Am. Chem. Soc.* **2010**, *132*, 17701–17703.
12. Bello, C. S.; Scgmidt-Leithoff, J. *Tetrahedron Lett.* **2012**, *53*, 6230–6235.