Palladium-Catalyzed Cross-Coupling Reaction of Diarylmethanol Derivatives with Diborylmethane

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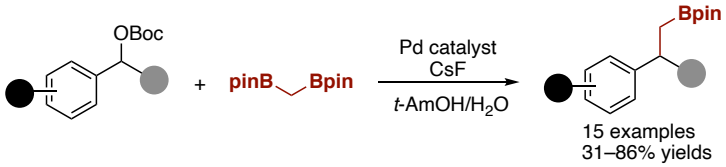
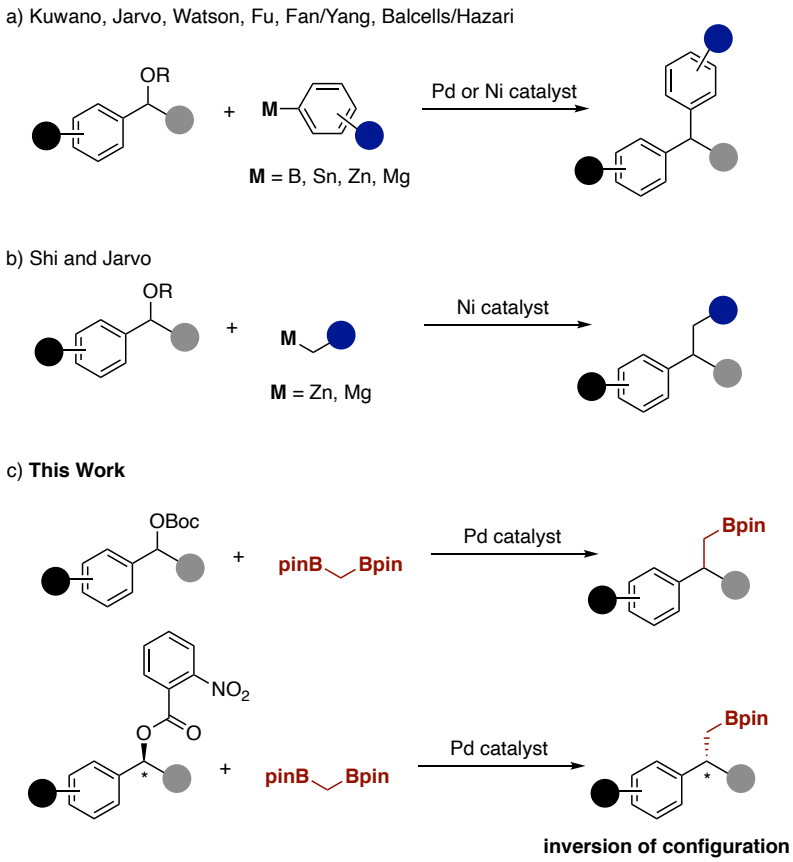


A palladium-catalyzed cross-coupling reaction of diarylmethanol derivatives with diborylmethane has been developed. The reaction proceeds chemoselectively to deliver the corresponding homobenzylic boronates in good yields.

Introduction

The transition-metal-catalyzed cross-coupling reaction of carbon electrophiles with organometallic reagents is now an indispensable synthetic technology for the carbon–carbon bond formation.[1] Traditionally, organic halides (C–X; X = I, Br, Cl) were employed as carbon electrophiles, but recent advances in transition metal catalysis and supporting ligands allow the readily available and stable but usually less reactive alcohol derivatives (C–O) to be adopted in the C–C bond forming cross-coupling reaction.[2] Among them, benzylic alcohol derivatives are relatively well studied as the reactive benzylic sp^3 carbon electrophiles by research groups of Kuwano,[3] Jarvo,[4] Watson,[5] Fu,[6] Fan/Yang,[7] and Balcells/Hazari,[8] and selective cross-coupling reactions with aryl organometallic reagents such as arylboranes, -tins, -zincs, and -magnesiums are possible under suitable Pd and Ni catalysis, giving di- and triarylmethane products (Scheme 1a). On the other hand, the application of alkyl metals still remains underdeveloped: only highly reactive dialkylzincs and alkylmagnesiums are successfully used in the presence of Ni catalysts, which was reported by Shi and co-workers[9a] and Jarvo and co-workers[9b-f] (Scheme 1b). Thus, further expansion of the scope of alkyl metal coupling partner in the cross-coupling reaction with benzylic C–O electrophiles is strongly appealing. Here, we report a palladium-catalyzed cross-coupling reaction of diarylmethyl carbonates with diborylmethane (Scheme 1c).[10,11] The reaction proceeds chemoselectively to form the corresponding homobenzylic boronates in good yields. Subsequent transformations of the remaining sp^3 C–B moiety successfully delivers the functionalized benzyl compounds. Moreover, the leaving-group-dependent chirality transfer from the enantioenriched diarylmethyl esters is also observed, providing the optically active cross-coupling product with the inversion of configuration.

Scheme 1. Transition-Metal-Catalyzed Cross-Coupling Reactions of Benzylic C–O Electrophiles; (a) Reactions with Arylmetals; (b) Reactions with Alkylmetals; (c) Reactions with Diborylmethane (This Work)

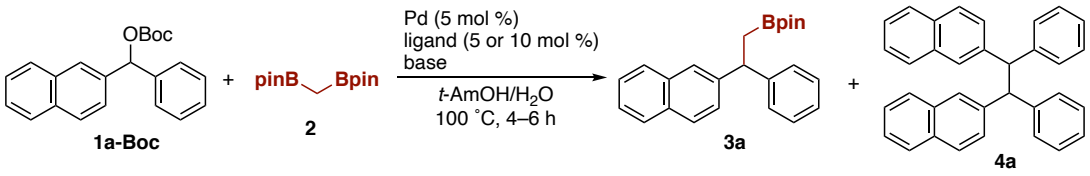


Results and Discussion

In recent years, our group has focused on the synthetic potential of benzylic C–O electrophiles and developed several palladium-catalyzed benzylic substitution reactions with carbon- and heteroatom-based nucleophiles.[12] During the continuing interest in this chemistry, we envisioned the C–C cross-coupling reaction with diborylmethane as the external carbon nucleophile. Our optimization studies commenced with *tert*-butyl diarylmethyl carbonate **1a-Boc** (0.20 mmol) and diborylmethane **2** (0.30 mmol; 1.5 equiv) to identify a suitable palladium catalyst precursor, ancillary ligand, base, and solvent. Representative results are shown in Table 1. The first trial using $[PdCl(\eta^3\text{-}C_3H_5)]_2$/P[3,5-(*t*-Bu)$_2$-4-MeO$C_6H_2$]$_3$ catalyst and K_2CO_3 base in a *t*-AmOH/H_2O (1:0.1, v/v) mixed solvent system (optimal conditions in our previous

Suzuki-type cross-coupling reaction)[12j] afforded the desired homobenzylic boronate **3a** in 16% ^{1}H NMR yield along with 5% of the homocoupling byproduct **4a** (entry 1). We then tested several monodentate (entries 2–7) and bidentate (entries 8–13) phosphine ligands. As a general trend, the monodentate phosphine ligand showed better performance, with a relatively simple P(4-MeC$_6$H$_4$)$_3$ proving to be the best as far as we tested (entry 6). Interestingly, low conversion of **1a-Boc** was observed in the presence of Pd[P(*t*-Bu)$_3$]$_2$ and PEPPSI-IPr (entries 14 and 15), which were optimal Pd catalysts in the related allylation and benzylation reactions of **2** with allyl and benzyl halides.[11a] Subsequent screening of palladium precursors (entries 16–19) revealed that Pd(OAc)$_2$ resulted in comparable efficiency with decreased homocoupling byproduct **4a** and better reproducibility (entry 16), and further studies were thus performed using the Pd(OAc)$_2$/P(4-MeC$_6$H$_4$)$_3$ combination. After investigations of bases and reaction stoichiometry (entries 20–23), the targeted **3a** was finally isolated in 86% yield with 5 mol % Pd(OAc)$_2$/P(4-MeC$_6$H$_4$)$_3$, 3.0 equiv **2**, and 4.5 equiv CsF (entry 23). Although the *tert*-butyl carbonate **1a-Boc** was the best from the viewpoint of reactivity, some other carbonates and related carboxylates could also be employed as the diarylmethyl electrophiles under identical conditions, except for the bulky **1a-Piv**, highly electron-deficient **1a-(NO$_2$)$_2$**, and heteroaromatic **1a-Py** (Scheme 2). In the case of **1a-Piv**, conversion was low, and the unreacted substrate was recovered in 65% yield. On the other hand, **1a-(NO$_2$)$_2$** and **1a-Py** mainly provided the corresponding carbinols probably via rapid hydrolysis of the ester moiety. Additional observations are to be noted: the both H$_2$O co-solvent and the external base were necessary for the satisfactory conversion of **1a-Boc**. Protic and aprotic solvents other than *t*-AmOH were also tested, but just leading to **2a** in lower yields. (see the Supporting Information for more detailed optimization studies).

Table 1. Optimization Studies for Palladium-Catalyzed Cross-Coupling Reaction of *tert*-Butyl Diarylmethyl Carbonate 1a-Boc with Diborylmethane 2[a]

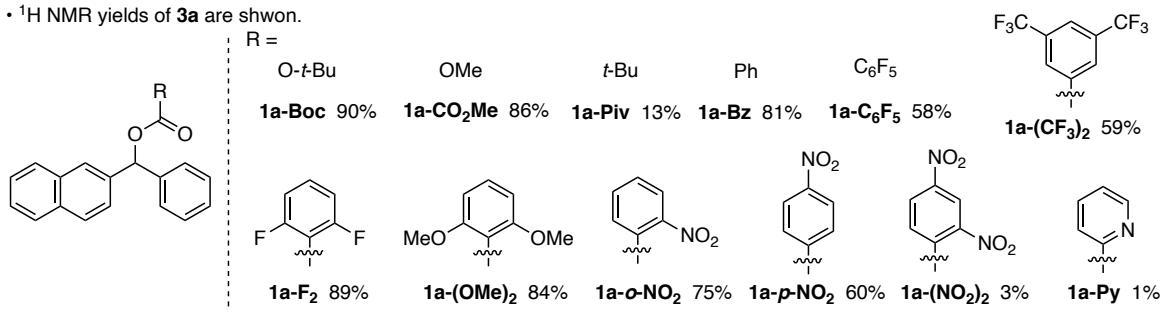


entry	Pd/ligand	base	yield (%)[b] 3a	4a
1	[PdCl(η^3-C_3H_5)]$_2$/P[3,5-(t-Bu)$_2$-4-MeOC_6H_2]$_3$	K_2CO_3	16	5
2	[PdCl(η^3-C_3H_5)]$_2$/P[3,5-(t-Bu)$_2C_6H_3$]$_3$	K_2CO_3	27	4
3	[PdCl(η^3-C_3H_5)]$_2$/P[3,5-(CF_3)$_2C_6H_3$]$_3$	K_2CO_3	0	trace
4	[PdCl(η^3-C_3H_5)]$_2$/PPh_3	K_2CO_3	56	24
5	[PdCl(η^3-C_3H_5)]$_2$/P(4-MeOC_6H_4)$_3$	K_2CO_3	42	28
6	[PdCl(η^3-C_3H_5)]$_2$/P(4-MeC_6H_4)$_3$	K_2CO_3	63	15
7	[PdCl(η^3-C_3H_5)]$_2$/P(4-FC_6H_4)$_3$	K_2CO_3	12	5
8	[PdCl(η^3-C_3H_5)]$_2$/dppbz	K_2CO_3	3	11
9	[PdCl(η^3-C_3H_5)]$_2$/dppe	K_2CO_3	4	5
10	[PdCl(η^3-C_3H_5)]$_2$/dppp	K_2CO_3	15	18
11	[PdCl(η^3-C_3H_5)]$_2$/dppb	K_2CO_3	48	33
12	[PdCl(η^3-C_3H_5)]$_2$/*rac*-BINAP	K_2CO_3	41	18
13	[PdCl(η^3-C_3H_5)]$_2$/dppf	K_2CO_3	33	48
14	Pd[P(t-Bu)$_3$]$_2$/none	K_2CO_3	11	1
15	PEPPSI-IPr/none	K_2CO_3	13	24
16	Pd(OAc)$_2$/P(4-MeC_6H_4)$_3$	K_2CO_3	69	7
17	$PdCl_2$/P(4-MeC_6H_4)$_3$	K_2CO_3	54	21
18	Pd_2(dba)$_3$/P(4-MeC_6H_4)$_3$	K_2CO_3	38	10

19	CpPd(η^3-C_3H_5)/P(4-MeC_6H_4)$_3$	K_2CO_3	43	10
20[c]	Pd(OAc)$_2$/P(4-MeC_6H_4)$_3$	K_2CO_3	84	5
21[c]	Pd(OAc)$_2$/P(4-MeC_6H_4)$_3$	KF	74	6
22[c]	Pd(OAc)$_2$/P(4-MeC_6H_4)$_3$	TBAF•3H_2O	11	44
23[c]	Pd(OAc)$_2$/P(4-MeC_6H_4)$_3$	CsF	90 (86)	5

[a] Conditions: **1a-Boc** (0.20 mmol), **2** (0.30 mmol), Pd (0.010 mmol), ligand (0.020 mmol for monodentate ligands and 0.010 mmol for bidentate ligands), base (0.90 mmol), *t*-AmOH/H_2O (1.0/0.10 mL), 100 ˚C, 4–6 h, N_2. [b] Estimated by ^{1}H NMR with 1-methylnaphthalene as the internal standard . Isolated yield in parentheses. [c] With **2** (0.60 mmol).

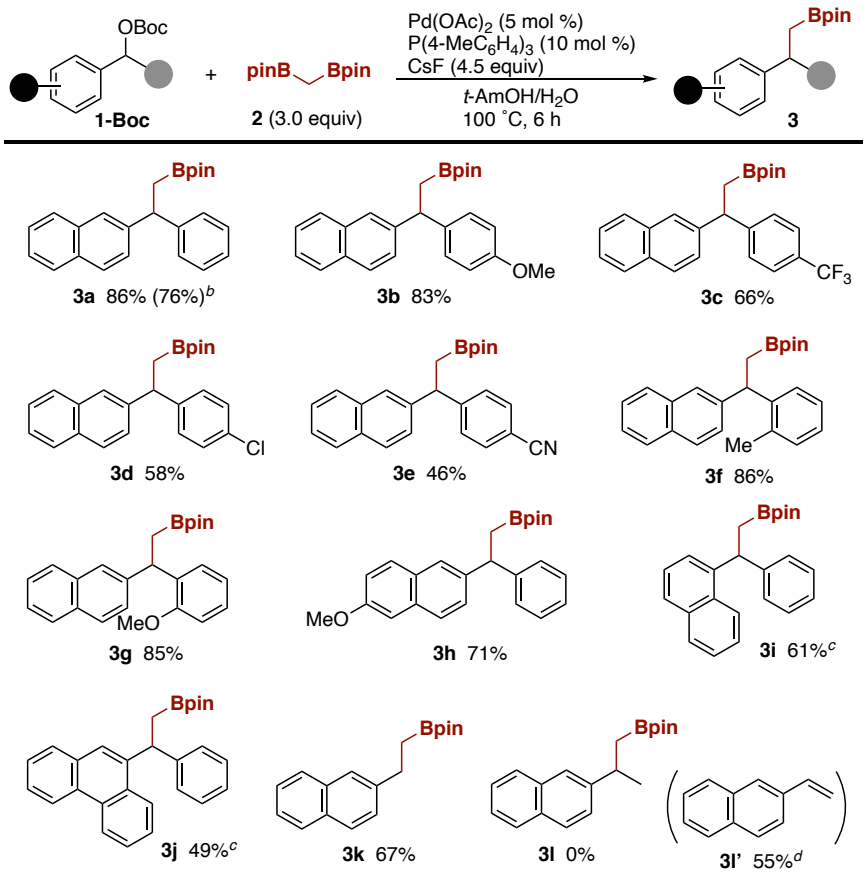
Scheme 2. Leaving Group Effects under Conditions of Entry 23 in Table 1



With the optimal conditions in hand, we next examined the scope of *tert*-butyl diarylmethyl carbonate **1-Boc** (Scheme 3). The reaction conditions were compatible with electron-donating methoxy (**3b**) and electron-withdrawing trifluoromethyl (**3c**) groups at the para-position on the phenyl ring. The Ar-Cl (**3d**) and Ar-CN (**3e**) functionalities were also tolerated. The palladium catalyst system accommodated the sterically hindered ortho-substituents (**3f** and **3g**). The 2-naphthyl group in the model substrate **1a-Boc** could be replaced with methoxy-substituted naphthyl, 1-naphthyl-, and higher fused phenanthryl groups to form the corresponding homobenzylic boronates **3h**–**j** in synthetically useful yields. The primary benzyl carbonate could also be employed without any difficulty (**3k**). The cross-coupling

reaction could also be performed on a 1.0 mmol scale (**3a**), thus indicating good reproducibility and scalability of the process. Unfortunately, attempts to apply the alkyl-substituted substrate remained unsuccessful: the targeted **3l** was not detected at all, and the corresponding 2-vinylnaphthalene (**3l'**) was instead formed probably via the β-H elimination of an alkylpalladium intermediate (vide infra).

Scheme 3. Palladium-Catalyzed Cross-Coupling Reaction of Various *tert*-Butyl Diarylmethyl Carbonates 1-Boc with Diborylmethane 2[a]

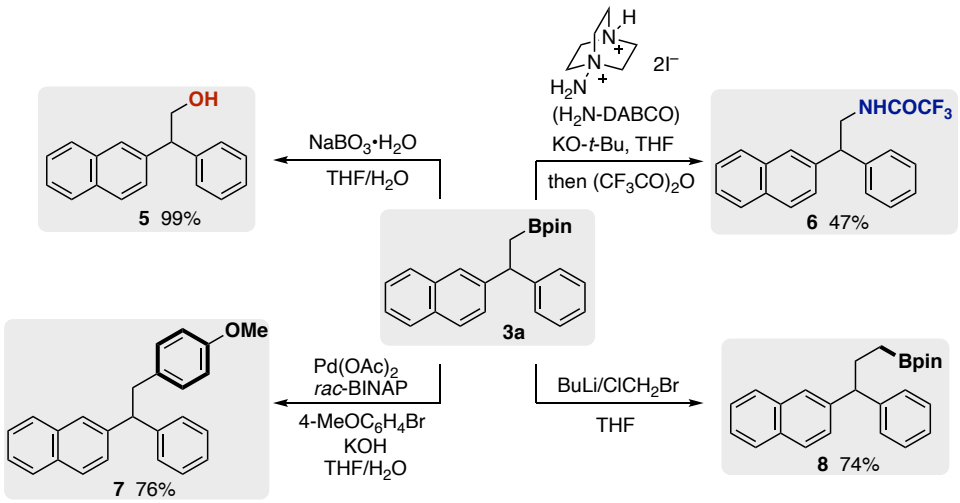


[a] Conditions: **1-Boc** (0.20 mmol), **2** (0.30 mmol), $Pd(OAc)_2$ (0.010 mmol), $P(4\text{-}MeC_6H_4)_3$ (0.020 mmol), CsF (0.90 mmol), *t*-AmOH/H_2O (1.0/0.10 mL), 100 ˚C, 6 h, N_2. Isolated yields are shown. [b] On a 1.0 mmol scale. [c] At 120 ˚C. [d] Estimated by ^1H NMR in the crude mixture.

The resulting C–Bpin moiety of the coupling product can be readily transformed through the established organoboron chemistry (Scheme 4). The corresponding alcohol **5** and amine **6** were easily prepared by oxidation and amination of **3a** with $NaBO_3$ and H_2N-DABCO,[13] respectively. The Suzuki-Miyaura

cross-coupling with 4-bromoanisole was also feasible in the presence of $Pd(OAc)_2$/*rac*-BINAP catalyst[14] to furnish **7** in 76% yield. Thus, the sequential Suzuki-Miyaura cross-coupling of diborylmethane **2** with sp^3 and sp^2 carbon electrophiles was possible under orthogonal conditions. Additionally, Matteson homologation with the in situ-generated lithium carbenoid[15] proceeded smoothly to deliver the bis-homobenzylic pinacol boronate **8** in a good yield.

Scheme 4. Derivatizations of Bpin Moiety of 3a[a]

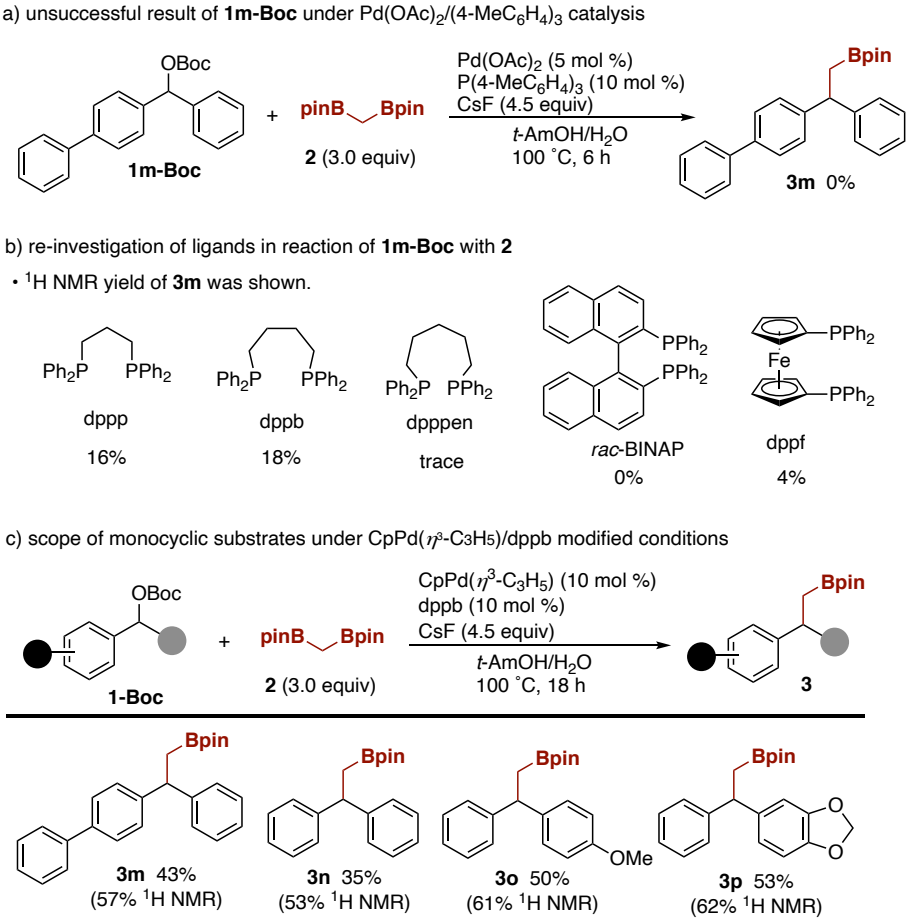


[a] See the Experimental Section for detailed conditions of each procedure.

As mentioned in Scheme 3, several naphthalene-derived diarylmethyl carbonates were successfully cross-coupled with **2** under Pd/P(4-MeC_6H_4)$_3$ catalysis. However, phenyl analogues, such as biphenyl-derived **1m-Boc**, underwent no conversion under identical conditions (Scheme 5a). A similar lower reactivity of monocyclic phenyl derivatives was often observed in related cross-coupling reactions of C–O electrophiles.[16] Thus, we re-investigated the Pd-based catalyst system with **1m-Boc** as the model substrate (Scheme 5b). Bidentate phosphine ligands that bear relatively large bite angle were mainly tested because they showed higher performance particularly in the related Pd-catalyzed Suzuki-Miyaura cross-coupling of simple diphenylmethyl carbonates with arylboronic acids.[3b] Actually, dppp and dppb promoted the reaction to some extent while dpppen, *rac*-BINAP, and dppf were unpromising. After

additional survey of other reaction parameters, we found that in the presence of 10 mol % of CpPd(η^3-C_3H_5)/dppb catalyst the targeted **3m** was formed with a synthetically acceptable level (57% ^{1}H NMR yield and 43% isolated yield; Scheme 5c). The modified catalyst system was uniquely effective[17] for some monocyclic substrates, including simple diphenylmethyl carbonate (**3n**) as well as its methoxy (**3o**) and methylenedioxy (**3p**) derivatives. In all cases, the conversion was good (>85%), but the competitive homocoupling reaction occurred (ca. 30%), which is like **4a** in Table 1, thus giving the desired cross-coupled products in moderate yields.

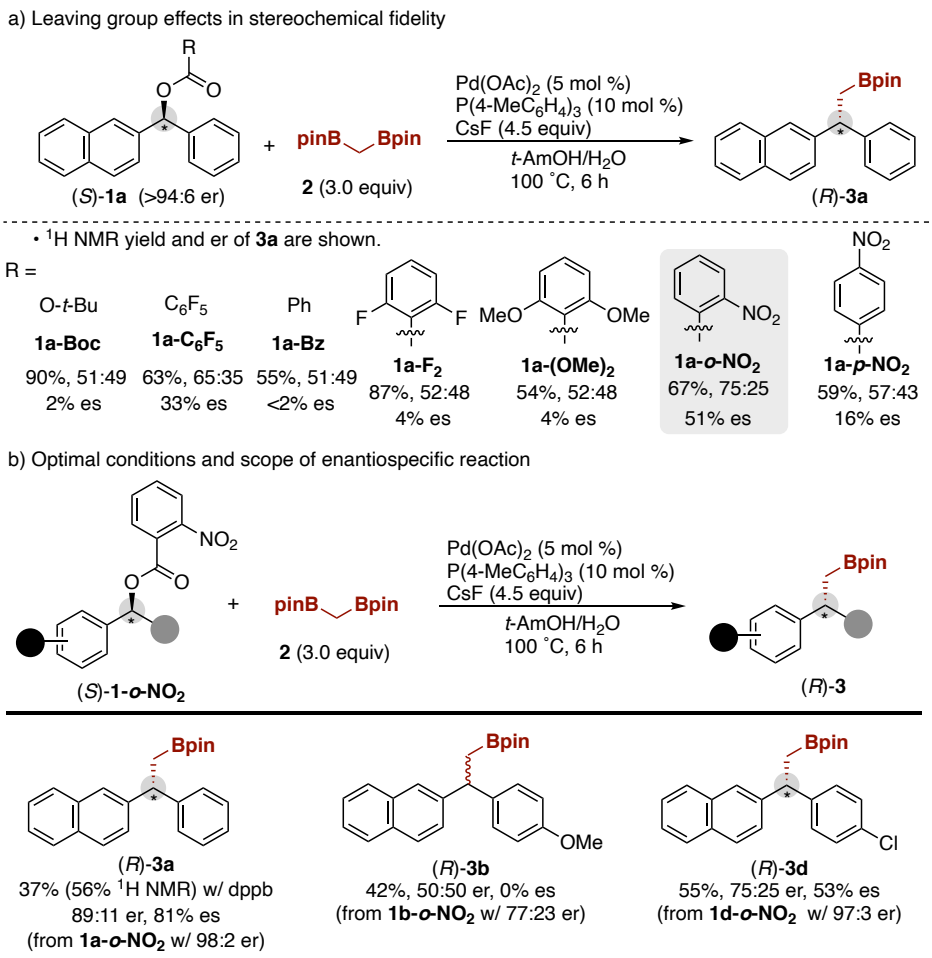
Scheme 5. Attempts To Apply Monocyclic Phenyl-Type Substrates



We finally attempted the enantiospecific cross-coupling reaction. When the independently prepared enantioenriched (*S*)-**1a-Boc**[18] was subjected to the standard conditions with Pd(OAc)$_2$/P(4-MeC$_6$H$_4$)$_3$ and CsF, the stereochemical information of the starting substrate was completely lost, and cross-coupled **3a**

was formed as a racemate (Scheme 6a; **1a-Boc,** 2% es). On the other hand, moderate but meaningful stereochemical fidelity was observed from (*S*)-**1a-C_6F_5**: the stereoinvertive (*R*)-**3a** was obtained albeit with a 65:35 enantiomeric ratio. This phenomenon prompted us to further investigate the leaving group effect on the enantiospecificity. The simple benzoate (*S*)-**1a-Bz**, moderately electron-deficient (*S*)-**1a-F_2**, and electron-rich (*S*)-**1a-$(MeO)_2$** all afforded **3a** in an almost racemic form, thus suggesting that the acidity of conjugate acid of the leaving group may play an important role in the stereochemical fidelity. Thus, we tried the reaction of highly electron-deficient (*S*)-**1a-*o*-NO_2**. Gratifyingly, the targeted (*R*)-**3a** was obtained with the highest 75:25 er. On the other hand, less electron-withdrawing *para*-isomer (*S*)-**1a-*p*-NO_2** diminished the enantiospecificity. Additional fine tuning of reaction conditions finally revealed that the combination of $Pd(OAc)_2$ and dppb showed the better stereochemical fidelity, and (*R*)-**3a** was formed with 89:11 er (81% es; Scheme 6b). The enantiospecific reaction was also applicable to the Cl-substituted (*S*)-**1d-*o*-NO_2**, in which the dppb ligand did not work well (only 4% ^{1}H NMR yield of **3d**; data not shown) and thus the standard conditions using $P(4\text{-}MeC_6H_4)_3$ were employed. On the other hand, the electron-donating MeO substituent was detrimental, and **3b** was formed as a racemate, probably because of rapid interconversion between two enantiomeric π-benzylpalladium intermediates (vide infra).[19]

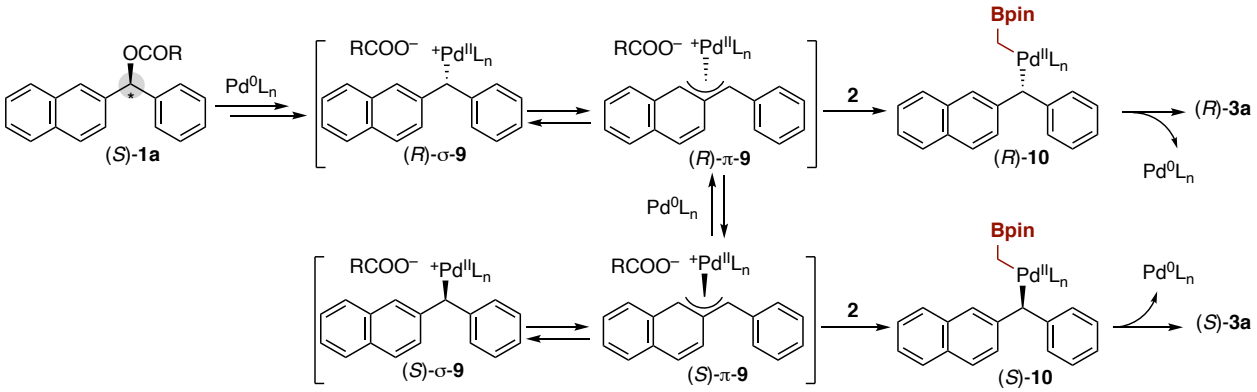
Scheme 6. Leaving-Group-Dependent Enantiospecific Reaction



Based on the aforementioned stereochemical findings and literature information, we are tempted to propose that the mechanism of reaction of (*S*)-**1a** with **2** is as follows (Scheme 7). Initially, $Pd(OAc)_2$ is reduced with diborylmethane **2** to form the catalytically active Pd^0L_n. The S_N2-type oxidative addition of Pd^0L_n to (*S*)-**1a** occurs with the inversion of configuration to initially form σ-benzylpalladium intermediate (*R*)-σ-**9**,[20] which is in equilibrium with π-benzyl isomer (*R*)-π-**9**.[16e] Subsequent transmetalation with **2** is followed by reductive elimination to furnish (*R*)-**3a** with an overall inversion of configuration. However, if the transmetalation process is slow, rapid racemization of point chirality at the benzylic position is feasible through interconversion between (*R*)-π-**9** and (*S*)-π-**9** by an S_N2-type back side attack of additional Pd^0L_n species.[21] As a result, an almost 1:1 mixture of (*R*)-**3a** and (*S*)-**3a** (racemate) is obtained. The results with (*S*)-**1a-Boc**, (*S*)-**1a-Bz**, (*S*)-**1a-F$_2$**, and (*S*)-**1a-(MeO)$_2$** are such cases. On the other hand, when (*S*)-**1a-C$_6$F$_5$** or (*S*)-**1a-*o*-NO$_2$** is employed, the transmetalation step

proceeds relatively smoothly because of the higher leaving ability of the corresponding weakly basic benzoate ion ($RCOO^-$ = $C_6F_5COO^-$ or *o*-$NO_2C_6H_4COO^-$). Accordingly, (*R*)-**3a** can be formed with significant stereochemical fidelity.[22] Actually, higher concentration of **2** increased the enantiospecificity, thus suggesting that the acceleration of transmetalation effectively suppresses the undesired racemization process through π-benzyl isomerization (see the Supporting Information for details). However, at this stage, the clear correlation between the enantiospecificity and the pK_a value of the conjugate acid of the leaving group was not observed: for example, the pK_a values of 2,6-$(MeO)_2C_6H_3COOH$ and 4-$NO_2C_6H_4COOH$ are the same (3.44),[23] but the enantiospecificity was totally different (4% es vs 16% es). Thus, additional investigations are necessary for the clarification of the detailed chirality transfer mechanism.

Scheme 7. Plausible Mechanism and Stereochemical Course



Conclusions

We have developed a palladium-based catalyst system for the chemoselective Suzuki-Miyaura cross-coupling reaction of diarylmethanol derivatives with diborylmethane.[24] The obtained product can be further manipulated via post functionalization of the remaining C–B bond. The palladium catalysis can provide a new repertoire of alkylmetal nucleophile in the cross-coupling reaction with readily available benzylic C–O electrophiles.

Experimental Section

Instrumentation and Chemicals ^{1}H, $^{13}C\{^{1}H\}$, $^{19}F\{^{1}H\}$, and ^{11}B NMR spectra were recorded at 400, 100, 376, and 128 MHz, respectively, for $CDCl_3$ solutions. High-resolution mass spectrometry (HRMS) data were obtained by APCI and electron ionization (EI) using time-of-flight (TOF) and a magnetic sector, respectively. Thin layer chromatgraphy analyses were performed on commercial glass plates bearing a 0.25 mm layer of Merck silica gel $60F_{254}$. Silica gel (60 N, spherical neutral, Kanto Chemical Co.) was used for column chromatography. Gel permeation chromatography (GPC) was performed using LC-20AR (pump, SHIMADZU, 7.5 mL/min) and SPD-20A (UV detector, SHIMADZU, 254 nm) with two in-line YMC-GPC T2000 (20 x 600 mm, particle size: 10 μm) (preparative columns, YMC). Chiral high-performance liquid chromatography (HPLC) analysis on a chiral stationary phase was performed using alliance (Waters e2695).

Unless otherwise noted, materials obtained from commercial suppliers were used without further purification. *t*-AmOH was dried on MS 5A and stored under nitrogen atmosphere. CpPd(η^3-C_3H_5) was prepared according to the literature.[25] All diarylmethanol derivatives **1** were synthesized from the corresponding carbinols.[12] All reactions were carried out under nitrogen atmosphere unless otherwise noted.

General Procedure for the Pd-Catalyzed Cross-Coupling Reaction of π-Extended Diarylmethanol Derivatives 1 with Diborylmethane 2. $Pd(OAc)_2$ (2.3 mg, 0.010 mmol, 5 mol %) and P(4-$MeC_6H_4)_3$ (6.1 mg, 0.020 mmol, 10 mol %) were placed in a 20 mL Schlenk tube, which was filled with nitrogen. *t*-AmOH (1.0 mL) was added to the reaction tube, and suspension was stirred for 10 min. Diarylmethyl carbonate (**1**; 0.20 mmol, 1.0 equiv), bis[(pinacolato)boryl]methane (**2**; 160.9 mg, 0.60 mmol, 3.0 equiv), CsF (136.6 mg, 0.90 mmol, 4.5 equiv), and H_2O (0.10 mL; *t*-AmOH:H_2O = 10:1, v/v) were then added to the reaction tube. The suspension was stirred for 6 h at 100 °C (oil bath). The resulting mixture was diluted with water and then extracted with ethyl acetate three times. The organic phase was filtered through a short pad of activated alumina and sodium sulfate. The filtrate was concentrated in vacuo. 1-

Methylnaphthalene was added as an internal standard, and the resulting mixture was analyzed by ^{1}H NMR in $CDCl_3$ solution. Concentration in vacuo and subsequent purification by column chromatography on neutral silica gel with hexane/ethyl acetate as an eluent gave the coupling product **3**. In some cases, additional purification by GPC was performed.

1.0 mmol Scale Synthesis of 3a. $Pd(OAc)_2$ (11.2 mg, 0.050 mmol, 5 mol %) and $P(4\text{-}MeC_6H_4)_3$ (30.4 mg, 0.100 mmol, 10 mol %) were placed in a 40 mL Schlenk tube, which was filled with nitrogen. *t*-AmOH (5.0 mL) was added to the reaction tube, and suspension was stirred for 10 min. *tert*-Butyl (2-naphthyl(phenyl)methyl) carbonate (**1a**; 334.5 mg, 1.0 mmol, 1.0 equiv), bis[(pinacolato)boryl]methane (**2**; 803.9 mg, 3.00 mmol, 3.0 equiv), CsF (683.7 mg, 4.50 mmol, 4.5 equiv), and H_2O (0.50 mL; *t*-AmOH:H_2O = 10:1, v/v) were then added to the reaction tube. The suspension was stirred for 6 h at 100 °C (oil bath). The resulting mixture was diluted with water and then extracted with ethyl acetate three times. The organic phase was filtered through a short pad of activated alumina and sodium sulfate. The filtrate was concentrated in vacuo. 1-Methylnaphthalene (10.8 mg) was added as an internal standard, and the resulting mixture was analyzed by ^{1}H NMR in $CDCl_3$ solution. Concentration in vacuo followed by silica gel column purification with hexane/ethyl acetate (20/1, v/v) and GPC (chloroform) gave 4,4,5,5-tetramethyl-2-(2-(naphthalen-2-yl)-2-phenylethyl)-1,3,2-dioxaborolane (**3a**; 273.4 mg, 0.76 mmol) in 76% yield.

4,4,5,5-Tetramethyl-2-(2-(naphthalen-2-yl)-2-phenylethyl)-1,3,2-dioxaborolane (3a). Purified by silica gel column chromatography with hexane/ethyl acetate (20/1, v/v): 61.3 mg (86%, 0.20 mmol scale); pale yellow solid; m.p. 60.3-61.3 °C; ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.79-7.74 (m, 3H), 7.70 (d, J = 8.5 Hz, 1H), 7.45-7.23 (m, 7H), 7.16-7.12 (m, 1H), 4.44 (t, J = 8.4 Hz, 1H), 1.71 (dd, J = 15.3, 8.5 Hz, 1H), 1.67 (dd, J = 15.3, 8.4 Hz, 1H), 1.039 (s, 6H), 1.034 (s, 6H). ^{13}C{^{1}H} NMR ($CDCl_3$, 100 MHz): δ 146.6, 144.2, 133.6, 132.2, 128.4, 127.98, 127.97, 127.9, 127.6, 127.1, 126.1, 125.9, 125.5, 125.3, 83.3, 46.7,

24.7. (The carbon signal bound to boron was not observed due to quadrupolar relaxation.) ^{11}B NMR ($CDCl_3$, 128 MHz): δ 33.8. HRMS (APCI) m/z $(M+H)^+$ calcd for $C_{24}H_{28}BO_2$: 359.2181, found: 359.2170.

2-(2-(4-Methoxyphenyl)-2-(naphthalen-2-yl)ethyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (3b). Purified by silica gel column chromatography with hexane/ethyl acetate (10/1, v/v): 63.9 mg (83%, 0.20 mmol scale); white solid; m.p. 87.7-88.7 °C; ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.79-7.69 (m, 4H), 7.45-7.38 (m, 2H), 7.33 (dd, J = 8.5 Hz, 1.6 Hz, 1H), 7.22 (d, J = 8.6 Hz, 2H), 6.81 (d, J = 8.6 Hz, 2H), 4.42 (t, J = 8.4 Hz, 1H), 3.76 (s, 3H), 1.69 (dd, J = 15.3, 8.4 Hz, 1H), 1.64 (dd, J = 15.3, 8.4 Hz, 1H), 1.06 (s, 12H). ^{13}C{^{1}H} NMR ($CDCl_3$, 100 MHz): δ 157.8, 144.5, 138.7, 133.5, 132.1, 128.8, 127.9, 127.7, 127.6, 126.9, 125.8, 125.24, 125.21, 113.7, 55.2, 45.8, 24.67, 24.65. (The carbon signal bound to boron was not observed due to quadrupolar relaxation.) ^{11}B NMR ($CDCl_3$, 128 MHz): δ 33.6. HRMS (APCI) m/z $(M)^+$ calcd for $C_{25}H_{29}BO_3$: 388.2209, found: 388.2228.

4,4,5,5-Tetramethyl-2-(2-(naphthalen-2-yl)-2-(4-(trifluoromethyl)phenyl)ethyl)-1,3,2-dioxaborolane (3c). Purified by silica gel column chromatography with hexane/ethyl acetate (10/1, v/v): 55.3 mg (66%, 0.20 mmol scale); yellow solid; m.p. 55.9-56.9 °C; ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.80-7.72 (m, 4H), 7.52 (d, J = 8.3 Hz, 2H), 7.48-7.41 (m, 4H), 7.32-7.29 (m, 1H), 4.52 (t, J = 8.3 Hz, 1H), 1.74 (dd, J = 15.4, 8.8 Hz, 1H), 1.67 (dd, J = 15.4, 8.2 Hz, 1H), 1.06 (s, 6H), 1.05 (s, 6H). ^{13}C{^{1}H} NMR ($CDCl_3$, 100 MHz): δ 150.6, 143.0, 133.5, 132.2, 128.3 (q, J = 31.4 Hz), 128.19, 128.15, 127.84, 127.76, 126.7, 126.1, 125.6, 125.5, 125.3 (q, J = 3.7 Hz), 124.3 (q, J = 270.0 Hz), 83.4, 46.4, 24.6. (The carbon signal bound to boron was not observed due to quadrupolar relaxation.) ^{11}B NMR ($CDCl_3$, 128 MHz): δ 34.3. ^{19}F{^{1}H} NMR ($CDCl_3$, 376 MHz): δ -62.30 (s). HRMS (APCI) m/z $(M)^+$ calcd for $C_{25}H_{26}BF_3O_2$: 426.1977, found: 426.2000.

2-(2-(4-Chlorophenyl)-2-(naphthalen-2-yl)ethyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (3d). Purified by silica gel column chromatography with hexane/ethyl acetate (20/1, v/v) and then by GPC (chloroform): 45.5 mg (58%, 0.20 mmol scale); pale yellow solid; m.p. 75.9-76.9 °C; ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.79-7.76 (m, 2H), 7.73-7.71 (m, 2H), 7.47-7.39 (m, 2H), 7.30 (dd, J = 8.6 Hz, 1.6 Hz, 1H), 7.25-7.21 (m, 4H), 4.43 (t, J = 8.3 Hz, 1H), 1.69 (dd, J = 15.3, 8.2 Hz, 1H), 1.63 (dd, J = 15.3, 8.4 Hz, 1H), 1.06 (s, 12H). ^{13}C{^{1}H} NMR ($CDCl_3$, 100 MHz): δ 145.1, 143.6, 133.5, 132.2, 131.8, 129.3, 128.5, 128.1, 127.8, 127.7, 126.8, 126.0, 125.5 (overlapping), 83.4, 46.0, 24.73, 24.71. (The carbon signal bound to boron was not observed due to quadrupolar relaxation.) ^{11}B NMR ($CDCl_3$, 128 MHz): δ 33.9. HRMS (APCI) m/z $(M)^+$ calcd for $C_{24}H_{26}BClO_2$: 392.1713, found: 392.1739.

4-(1-(Naphthalen-2-yl)-2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)ethyl)benzonitrile (3e). Purified by silica gel column chromatography with hexane/ethyl acetate (10/1, v/v): 35.5 mg (46%, 0.20 mmol scale); white solid; m.p. 85.2-86.2 °C; ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.80-7.76 (m, 2H), 7.73 (d, J = 8.2 Hz, 2H), 7.56-7.54 (m, 2H), 7.48-7.43 (m, 2H), 7.40 (d, J = 8.2 Hz, 2H), 7.26 (dd, J = 8.7, 1.9 Hz, 1H), 4.50 (t, J = 8.4 Hz, 1H), 1.71 (dd, J = 15.5, 8.4 Hz, 1H), 1.65 (dd, J = 15.5, 8.4 Hz, 1H), 1.05 (s, 12H). ^{13}C{^{1}H} NMR ($CDCl_3$, 100 MHz): δ 152.1, 142.4, 133.4, 132.2 (overlapping), 128.7, 128.3, 127.7, 127.6, 126.5, 126.2, 125.7, 125.6, 119.1, 109.8, 83.4, 46.7, 24.63, 24.61. (The carbon signal bound to boron was not observed due to quadrupolar relaxation.) ^{11}B NMR ($CDCl_3$, 128 MHz): δ 34.1. HRMS (APCI) m/z $(M+H)^+$ calcd for $C_{25}H_{27}BNO_2$: 384.2134, found: 384.2146.

4,4,5,5-Tetramethyl-2-(2-(naphthalen-2-yl)-2-(*o*-tolyl)ethyl)-1,3,2-dioxaborolan (3f). Purified by silica gel column chromatography with hexane/ethyl acetate (10/1, v/v): 61.3 mg (86%, 0.20 mmol scale); yellow solid; m.p. 73.6-74.6 °C; ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.78-7.75 (m, 2H), 7.72-7.68 (m, 2H), 7.45-7.38 (m, 3H), 7.35-7.33 (m, 1H), 7.23-7.19 (m, 1H), 7.12-7.11 (m, 2H), 4.66 (t, J = 8.3 Hz, 1H), 2.35 (s, 3H), 1.69 (dd, J = 15.7, 8.3 Hz, 1H), 1.66 (dd, J = 15.7, 8.7 Hz, 1H), 1.09 (s, 6H), 1.04 (s, 6H).

$^{13}C\{^{1}H\}$ NMR ($CDCl_3$, 100 MHz): δ 144.00, 143.97, 136.2, 133.4, 132.0, 130.3, 127.8, 127.7, 127.5, 127.1, 126.9, 126.04, 125.99, 125.8, 125.7, 125.2, 83.2, 42.5, 24.6, 20.0. (The carbon signal bound to boron was not observed due to quadrupolar relaxation.) ^{11}B NMR ($CDCl_3$, 128 MHz): δ 34.2. HRMS (APCI) m/z $(M)^+$ calcd for $C_{25}H_{29}BO_2$: 372.2260, found: 372.2265.

2-(2-(2-Methoxyphenyl)-2-(naphthalen-2-yl)ethyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (3g). Purified by silica gel column chromatography with hexane/ethyl acetate (10/1, v/v): 65.5 mg (85%, 0.20 mmol scale); pale yellow solid; m.p. 80.6-81.6 °C; ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.78-7.74 (m, 3H), 7.69 (d, J = 8.6 Hz, 1H), 7.43-7.39 (m, 3H), 7.30 (dd, J = 7.6, 1.6 Hz, 1H), 7.15 (td, J = 7.7, 1.7 Hz, 1H), 6.91 (td, J = 7.5, 1.1 Hz, 1H), 6.82 (dd, J = 8.2, 1.0 Hz, 1H), 4.89 (t, J = 8.6 Hz, 1H), 3.77 (s, 3H), 1.69 (dd, J = 15.2, 8.7 Hz, 1H), 1.65 (dd, J = 15.2, 9.2 Hz, 1H), 1.032 (s, 6H), 1.028 (s, 6H). $^{13}C\{^{1}H\}$ NMR ($CDCl_3$, 100 MHz): δ 159.9, 144.2, 134.9, 133.5, 132.0, 127.9, 127.7, 127.5, 127.4, 127.3, 127.0, 125.6, 125.5, 124.9, 120.4, 110.6, 83.2, 55.5, 39.2, 24.61, 24.58. (The carbon signal bound to boron was not observed due to quadrupolar relaxation.) ^{11}B NMR ($CDCl_3$, 128 MHz): δ 34.1. HRMS (APCI) m/z $(M)^+$ calcd for $C_{25}H_{29}BO_3$: 388.2209, found: 388.2228.

2-(2-(6-Methoxynaphthalen-2-yl)-2-phenylethyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (3h). Purified by silica gel column chromatography with hexane/ethyl acetate (10/1, v/v): 54.9 mg (71%, 0.20 mmol scale); white solid; m.p. 89.9-90.9 °C; ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.69-7.67 (m, 2H), 7.61 (d, J = 8.5 Hz, 1H), 7.32-7.29 (m, 3H), 7.27-7.23 (m, 2H), 7.16-7.07 (m, 3H), 4.42 (t, J = 8.4 Hz, 1H), 3.89 (s, 3H), 1.70 (dd, J = 15.3, 8.6 Hz, 1H), 1.65 (dd, J = 15.3, 8.3 Hz, 1H), 1.04 (s, 6H), 1.04 (s, 6H). $^{13}C\{^{1}H\}$ NMR ($CDCl_3$, 100 MHz): δ 157.2, 146.7, 141.8, 133.1, 129.2, 128.9, 128.3, 127.8, 127.4, 126.8, 125.9, 125.3, 118.5, 105.6, 83.2, 55.3, 46.4, 24.6. (The carbon signal bound to boron was not observed due to quadrupolar relaxation.) ^{11}B NMR ($CDCl_3$, 128 MHz): δ 33.7. HRMS (APCI) m/z $(M+H)^+$ calcd for $C_{25}H_{30}BO_3$: 389.2287, found: 389.2287.

4,4,5,5-Tetramethyl-2-(2-(naphthalen-1-yl)-2-phenylethyl)-1,3,2-dioxaborolane (3i). Purified by silica gel column chromatography with hexane/ethyl acetate (20/1, v/v): 43.7 mg (61%, 0.20 mmol scale); pale yellow solid; m.p. 87.9-88.9 °C; ^{1}H NMR ($CDCl_3$, 400 MHz): δ 8.19-8.16 (m, 1H), 7.83-7.79 (m, 1H), 7.71 (d, J = 8.1 Hz, 1H), 7.53 (d, J = 6.4 Hz, 1H), 7.47-7.39 (m, 3H), 7.32-7.29 (m, 2H), 7.24-7.20 (m, 2H), 7.14-7.09 (m, 1H), 5.10 (t, J = 8.3 Hz, 1H), 1.75 (dd, J = 15.3, 8.2 Hz, 1H), 1.70 (dd, J = 15.3, 8.4 Hz, 1H), 1.07 (s, 6H), 0.99 (s, 6H). ^{13}C{^{1}H} NMR ($CDCl_3$, 100 MHz): δ 146.9, 142.0, 134.0, 131.8, 128.6, 128.3, 127.8, 126.9, 125.9, 125.7, 125.4, 125.3, 124.4, 124.3, 83.2, 42.0, 24.6. (The carbon signal bound to boron was not observed due to quadrupolar relaxation.) ^{11}B NMR ($CDCl_3$, 128 MHz): δ 34.2. HRMS (APCI) m/z $(M)^+$ calcd for $C_{24}H_{27}BO_2$: 358.2103, found: 358.2131.

4,4,5,5-Tetramethyl-2-(2-(phenanthren-9-yl)-2-phenylethyl)-1,3,2-dioxaborolane (3j). Purified by silica gel column chromatography with hexane/ethyl acetate (20/1, v/v): 40.0 mg (49%, 0.20 mmol scale); pale yellow solid; m.p. 127.2-128.2 °C; ^{1}H NMR ($CDCl_3$, 400 MHz): δ 8.70 (d, J = 7.8 Hz, 1H), 8.65 (d, J = 8.2 Hz, 1H), 8.16 (d, J = 8.3 Hz, 1H), 7.91-7.89 (m, 1H), 7.82 (s, 1H), 7.64-7.56 (m, 3H), 7.52-7.48 (m, 1H), 7.33 (d, J = 7.8 Hz, 2H), 7.22 (t, J = 7.8 Hz, 2H), 7.14-7.10 (m, 1H), 5.07 (t, J = 8.2 Hz, 1H), 1.84 (dd, J = 15.4, 8.4 Hz, 1H), 1.73 (dd, J = 15.4, 8.0 Hz, 1H), 1.09 (s, 6H), 1.00 (s, 6H). ^{13}C{^{1}H} NMR ($CDCl_3$, 100 MHz): δ 146.9, 139.7, 131.7, 131.2, 130.8, 129.8, 128.6, 128.4, 127.7, 126.6, 126.4, 126.2, 125.94, 125.93, 125.2, 125.1, 123.0, 122.4, 83.2, 42.6, 24.7, 24.6. (The carbon signal bound to boron was not observed due to quadrupolar relaxation.) ^{11}B NMR ($CDCl_3$, 128 MHz): δ 34.5. HRMS (APCI) m/z $(M)^+$ calcd for $C_{28}H_{29}BO_2$: 408.2260, found: 408.2261.

4,4,5,5-Tetramethyl-2-(2-(naphthalen-2-yl)ethyl)-1,3,2-dioxaborolane (3k). Purified by silica gel column chromatography with hexane/ethyl acetate (20/1, v/v): 38.0 mg (67%, 0.20 mmol scale); white solid; m.p. 53.3-54.3 °C; ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.79-7.73 (m, 3H), 7.64 (s, 1H), 7.45-7.36 (m,

3H), 2.91 (t, J = 8.2 Hz, 2H), 1.25-1.22 (m, 14H). $^{13}C\{^{1}H\}$ NMR ($CDCl_3$, 100 MHz): δ 142.0, 133.7, 131.9, 127.7, 127.6, 127.4, 127.3, 125.72, 125.70, 124.9, 83.1, 30.1, 24.8. (The carbon signal bound to boron was not observed due to quadrupolar relaxation.) ^{11}B NMR ($CDCl_3$, 128 MHz): δ 34.3. HRMS (APCI) m/z $(M)^+$ calcd for $C_{18}H_{23}BO_2$: 282.1789, found: 282.1796.

General Procedure for the Pd-Catalyzed Cross-Coupling Reaction of Monocyclic Phenyl-Type Diarylmethanol Derivatives 1 with Diborylmethane 2. 1,4-Bis(diphenylphosphino)butane (dppb; 8.5 mg, 0.020 mmol, 10 mol %) was placed in a 20 mL Schlenk tube in a glovebox filled with nitrogen. CpPd(η^3-C_3H_5) (4.4 mg, 0.020 mmol, 10 mol %) and *t*-AmOH (1.0 mL) were added to the reaction tube, and suspension was stirred for 10 min. CsF (136.8 mg, 0.90 mmol, 4.5 equiv) was added to the reaction tube. The reaction tube was sealed with a septum and taken out of the glovebox. Diarylmethyl carbonate (**1**; 0.20 mmol, 1.0 equiv), bis[(pinacolato)boryl]methane (**2**; 160.8 mg, 0.60 mmol, 3.0 equiv), and H_2O (0.10 mL; *t*-AmOH:H_2O = 10:1, v/v) were then added to the reaction tube. The suspension was stirred for 6 h at 100 °C (oil bath). The resulting mixture was diluted with water and then extracted with ethyl acetate three times. The organic phase was filtered through a short pad of activated alumina and sodium sulfate. The filtrate was concentrated in vacuo. 1-Methylnaphthalene was added as an internal standard, and the resulting mixture was analyzed by ^1H NMR in $CDCl_3$ solution. Concentration in vacuo and subsequent purification by column chromatography on neutral silica gel with hexane/ethyl acetate as an eluent gave the coupling product **3**. In some cases, additional purification by GPC was performed.

2-(2-([1,1'-Biphenyl]-4-yl)-2-phenylethyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (3m). Purified by silica gel column chromatography with hexane/ethyl acetate (20/1, v/v) and then by GPC (ethyl acetate): 33.2 mg (43%, 0.20 mmol scale); pale yellow solid; m.p. 99.6-100.6 °C; ^1H NMR ($CDCl_3$, 400 MHz): δ 7.56-7.54 (m, 2H), 7.48 (d, J = 8.3 Hz, 2H), 7.42-7.38 (m, 2H), 7.34-7.28 (m, 6H), 7.27-7.25 (m, 1H), 7.17-7.13 (m, 1H), 4.32 (t, J = 8.5 Hz, 1H), 1.63 (d, J = 8.5 Hz, 2H), 1.061 (s, 6H), 1.058 (s, 6H).

$^{13}C\{^{1}H\}$ NMR ($CDCl_3$, 100 MHz): δ 146.5, 145.8, 141.1, 138.8, 128.7, 128.3, 128.1, 127.7, 127.0 (overlapping, 3C), 126.0, 83.2, 46.2, 24.6. (The carbon signal bound to boron was not observed due to quadrupolar relaxation.) ^{11}B NMR ($CDCl_3$, 128 MHz): δ 34.2. HRMS (APCI) m/z $(M)^+$ calcd for $C_{26}H_{29}BO_2$: 384.2260, found: 384.2240.

2-(2,2-Diphenylethyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (3n). Purified by silica gel column chromatography with hexane/ethyl acetate (20/1, v/v): 21.9 mg (35%, 0.20 mmol scale); yellow solid; m.p. 66.7-67.7 °C; ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.28-7.22 (m, 8H), 7.15-7.11 (m, 2H), 4.28 (t, J = 8.5 Hz, 1H), 1.60 (d, J = 8.5 Hz, 2H), 1.05 (s, 12H). $^{13}C\{^{1}H\}$ NMR ($CDCl_3$, 100 MHz): δ 146.6, 128.2, 127.7, 125.9, 83.1, 46.5, 24.6. (The carbon signal bound to boron was not observed due to quadrupolar relaxation.) ^{11}B NMR ($CDCl_3$, 128 MHz): δ 33.8. HRMS (APCI) m/z $(M+H)^+$ calcd for $C_{20}H_{26}BO_2$: 309.2024, found:309.2045.

2-(2-(4-Methoxyphenyl)-2-phenylethyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (3o). Purified by silica gel column chromatography with hexane/ethyl acetate (20/1, v/v): 34.0 mg (50%, 0.20 mmol scale); orange solid; m.p. 65.9-66.9 °C; ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.25-7.21 (m, 4H), 7.18 (dt, J = 8.6, 2.0 Hz, 2H), 7.14-7.10 (m, 1H), 6.79 (dt, J = 8.7, 2.1 Hz, 2H), 4.23 (t, J = 8.5 Hz, 1H), 3.75 (s, 3H), 1.57 (d, J = 8.4 Hz, 2H), 1.06 (s, 12H). $^{13}C\{^{1}H\}$ NMR ($CDCl_3$, 100 MHz): δ 157.8, 147.0, 138.9, 128.6, 128.2, 127.6, 125.8, 113.6, 83.1, 55.2, 45.7, 24.62, 24.60. (The carbon signal bound to boron was not observed due to quadrupolar relaxation.) ^{11}B NMR ($CDCl_3$, 128 MHz): δ 33.3. HRMS (APCI) m/z $(M)^+$ calcd for $C_{21}H_{27}BO_3$: 338.2052, found:338.2044.

2-(2-(Benzo[*d*][1,3]dioxol-5-yl)-2-phenylethyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (3p). Purified by silica gel column chromatography with hexane/ethyl acetate (10/1, v/v) and then by GPC (ethyl acetate): 37.1 mg (53%, 0.20 mmol scale); yellow solid; m.p. 70.3-71.3 °C; ^{1}H NMR ($CDCl_3$, 400

MHz): δ 7.25-7.22 (m, 4H), 7.17-7.11 (m, 1H), 6.78-6.68 (m, 3H), 5.88 (s, 2H), 4.20 (t, J = 8.4 Hz, 1H), 1.56 (dd, J = 17.0, 8.5 Hz, 1H), 1.52 (dd, J = 17.4, 8.5 Hz, 1H), 1.073 (s, 6H), 1.070 (s, 6H). $^{13}C\{^1H\}$ NMR ($CDCl_3$, 100 MHz): δ 147.5, 146.6, 145.6, 140.8, 128.3, 127.5, 126.0, 120.4, 108.3, 107.9, 100.7, 83.2, 46.2, 24.62, 24.61. (The carbon signal bound to boron was not observed due to quadrupolar relaxation.) ^{11}B NMR ($CDCl_3$, 128 MHz): δ 33.3. HRMS (APCI) m/z $(M)^+$ calcd for $C_{21}H_{25}BO_4$: 352.1844, found: 352.1834.

General Procedure for the Pd-Catalyzed Enantiospecific Cross-Coupling Reaction of Diarylmethanol Derivatives 1 with Diborylmethane 2. $Pd(OAc)_2$ (2.3 mg, 0.010 mmol, 5 mol %) and $P(4\text{-}MeC_6H_4)_3$ (6.1 mg, 0.020 mmol, 10 mol %) or dppb (4.3 mg, 0.010 mmol, 5 mol %) were placed in a 20 mL Schlenk tube, which was filled with nitrogen. *t*-AmOH (1.0 mL) was added to the reaction tube, and suspension was stirred for 10 min. Optically active diarylmethyl 2-nitrobenzoate (**1-*o*-NO$_2$**; 0.20 mmol, 1.0 equiv), bis[(pinacolato)boryl]methane (160.6 mg, 0.60 mmol, 3.0 equiv), CsF (137.0 mg 0.90 mmol, 4.5 equiv), and H_2O (0.10 mL; *t*-AmOH:H_2O = 10:1, v/v) were then added to the reaction tube. The suspension was stirred for 6 h at 100 °C (oil bath). The resulting mixture was diluted with water and then extracted with ethyl acetate three times. The organic phase was filtered through a short pad of activated alumina and sodium sulfate. The filtrate was concentrated in vacuo. 1-Methylnaphthalene was added as an internal standard, and the resulting mixture was analyzed by ^1H NMR in $CDCl_3$ solution. Concentration in vacuo and subsequent purification by column chromatography on neutral silica gel with hexane/ethyl acetate and GPC (chloroform) as an eluent gave (*R*)-**3**. The absolute configuration was assigned by the comparison of specific rotation of (*R*)-**3a** (75:25 er, $[\alpha]_D^{20}$ –5.31 (c 0.245, $CHCl_3$)) with the reported value.[14]

Procedure for Oxidation of 3a. 4,4,5,5-Tetramethyl-2-(2-(naphthalen-2-yl)-2-phenylethyl)-1,3,2-dioxaborolane (**3a**; 53.8 mg, 0.15 mmol) and $NaBO_3 \cdot OH_2$ (229.4 mg, 2.3 mmol) were placed in a 20 mL

round-bottom flask. Tetrahydrofuran (THF)/H_2O (1.0 mL/1.0 mL) was added to the flask, and the resulting mixture was stirred for 7 h at room temperature under air. The reaction was quenched with sat. $Na_2S_2O_3$ aq. The resulting mixture was directly filtered through a pad of sodium sulfate and concentrated in vacuo. The residue was purified by column chromatography on neutral silica gel with hexane/ethyl acetate (3/1) as an eluent to give 2-(naphthalen-2-yl)-2-phenylethan-1-ol (**5**; 37.0 mg, 0.15 mmol) in 99% yield.

2-(Naphthalen-2-yl)-2-phenylethan-1-ol (5). Purified by silica gel column chromatography with hexane/ethyl acetate (3/1, v/v): 37.0 mg (99%, 0.15 mmol scale); white solid; m.p. 65.3-66.3 ^oC; ^1H NMR ($CDCl_3$, 400 MHz): δ 7.81-7.77 (m, 3H), 7.74 (s, 1H), 7.49-7.42 (m, 2H), 7.37-7.29 (m, 5H), 7.26-7.22 (m, 1H), 4.38 (t, J = 7.1 Hz, 1H), 4.32-4.22 (m, 2H), 1.56-1.53 (m, 1H). $^{13}C\{^1H\}$ NMR ($CDCl_3$, 100 MHz): δ 141.3, 138.8, 133.5, 132.4, 128.8, 128.5, 128.4, 127.8, 127.6, 126.91, 126.85, 126.6, 126.2, 125.8, 66.1, 53.7. HRMS (EI+) m/z $(M)^+$ calcd for $C_{18}H_{16}O$: 248.1196, found: 248.1205.

Procedure for Amination of 3a. 4,4,5,5-Tetramethyl-2-(2-(naphthalen-2-yl)-2-phenylethyl)-1,3,2-dioxaborolane (**3a**; 53.8 mg, 0.15 mmol) and NH_2-DABCO (57.8 mg, 0.15 mmol) were placed in a 10 mL microwave reaction vessel in a glovebox filled with nitrogen. KO-*t*-Bu (40.7 mg, 0.36 mmol) and THF (1.8 mL) were added to the reaction tube. The reaction tube was sealed with a cap and taken out of the glovebox, and the resulting mixture was stirred for 3 h at 100 ℃ (oil bath). TFAA (42 μL, 0.30 mmol) was then added, and the reaction mixture was heated at 100 ℃ for additional 1 h (oil bath). The reaction was quenched with ethyl acetate and H_2O, and the mixture was directly filtered through a pad of sodium sulfate. Concentration in vacuo and subsequent purification by column chromatography on neutral silica gel with hexane/ethyl acetate (5/1) as an eluent gave 2,2,2-trifluoro-*N*-(2-(naphthalen-2-yl)-2-phenylethyl)acetamide (**6**; 24.0 mg, 0.070 mmol) in 47% yield.

2,2,2-Trifluoro-*N*-(2-(naphthalen-2-yl)-2-phenylethyl)acetamide (6). Purified by silica gel column chromatography with hexane/ethyl acetate (5/1, v/v): 24.0 mg (47%, 0.15 mmol scale); white solid; m.p. 94.0-95.0 °C; ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.82-7.80 (m, 3H), 7.71 (s, 1H), 7.52-7.45 (m, 2H), 7.37-7.27 (m, 6H), 6.21 (br, 1H), 4.40 (t, J = 8.0 Hz, 1H), 4.16-4.05 (m, 2H). ^{13}C{^{1}H} NMR ($CDCl_3$, 100 MHz): δ 157.2 (q, J = 37.6 Hz), 140.7, 138.1, 133.4, 132.5, 129.0, 128.9, 128.0, 127.8, 127.7, 127.4, 126.5, 126.21, 126.18, 126.1, 115.7 (q, J = 284.7 Hz), 50.0, 43.9. ^{19}F{^{1}H} NMR ($CDCl_3$, 376 MHz): δ -76.00 (s). HRMS (APCI) m/z $(M+H)^+$ calcd for $C_{20}H_{17}F_3NO$: 344.1257, found: 344.1264.

Procedure for Suzuki-Miyaura Cross-Coupling of 3a. 4,4,5,5-Tetramethyl-2-(2-(naphthalen-2-yl)-2-phenylethyl)-1,3,2-dioxaborolane (**3a**; 53.8 mg, 0.15 mmol) and KOH (126.4 mg, 2.25 mmol) were placed in a 20 mL Schlenk tube in a glovebox filled with nitrogen. 1-Bromo-4-methoxybenzene (84.0 mg, 0.45 mmol) in THF (1.0 mL), and *rac*-BINAP (14.0 mg, 0.0225 mmol) and $Pd(OAc)_2$ (5.1 mg, 0.0225 mmol) in THF (1.0 mL) were sequentially added to the reaction tube. The reaction tube was sealed with a septum and taken out of the glovebox. H_2O (0.20 mL) was finally added to the reaction tube. The suspension was stirred for 12 h at 100 °C (oil bath). The resulting mixture was filtered through a short pad of activated alumina and sodium sulfate, and the filtrate was concentrated in vacuo. 1-Methylnaphthalene (14.0 mg) was added as an internal standard, and the resulting mixture was analyzed by ^{1}H NMR in $CDCl_3$ solution. Concentration in vacuo and subsequent purification by column chromatography on neutral silica gel with hexane/ethyl acetate (20/1) and GPC (chloroform) as an eluent gave 2-(2-(4-methoxyphenyl)-1-phenylethyl)naphthalene (**7**; 38.6 mg, 0.11 mmol) in 76% yield.

2-(2-(4-Methoxyphenyl)-1-phenylethyl)naphthalene (7). Purified by silica gel column chromatography with hexane/ethyl acetate (20/1, v/v) and then by GPC (chloroform): 38.6 mg (76%, 0.15 mmol scale); pale yellow solid; m.p. 76.7-77.7 °C; ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.80-7.76 (m, 2H), 7.74 (d, J = 8.6 Hz, 1H), 7.68 (s, 1H), 7.47-7.41 (m, 2H), 7.35 (d, J = 8.5 Hz, 1H), 7.29-7.25 (m, 4H),

7.21-7.16 (m, 1H), 6.95 (d, J = 8.5 Hz, 2H), 6.72 (d, J = 8.4 Hz, 2H), 4.37 (t, J = 7.7 Hz, 1H), 3.74 (s, 3H), 3.46 (dd, J = 13.8, 9.0 Hz, 1H), 3.40 (dd, J = 13.8 Hz, 7.8 Hz, 1H). $^{13}C\{^{1}H\}$ NMR ($CDCl_3$, 100 MHz): δ 157.8, 144.5, 142.0, 133.5, 132.3, 132.2, 130.0, 128.4, 128.2, 128.0, 127.8, 127.6, 127.0, 126.3, 126.2, 125.9, 125.4, 113.5, 55.2, 53.4, 41.1. HRMS (EI+) m/z $(M)^+$ calcd for $C_{25}H_{22}O$: 338.1665, found: 338.1664.

Procedure for Matteson Homologation of 3a. To a solution of 4,4,5,5-tetramethyl-2-(2-(naphthalen-2-yl)-2-phenylethyl)-1,3,2-dioxaborolane (**3a**; 53.7 mg, 0.15 mmol) and bromochloromethane (38.7 mg, 0.30 mmol) in THF (1.5 mL) at -78 ℃ was added *n*-BuLi (1.56 M hexane solution, 0.16 mL, 0.25 mmol), and the solution was stirred at the same temperature for 30 min. The mixture was allowed to warm to room temperature over 30 min and then heated at 60 ℃ for additional 3 h (oil bath). The resulting mixture was quenched with NH_4Cl and extracted with ethyl acetate. The combined organic layer was dried over sodium sulfate and concentrated in vacuo. The residue was purified by GPC (chloroform) gave 4,4,5,5-tetramethyl-2-(3-(naphthalen-2-yl)-3-phenylpropyl)-1,3,2-dioxaborolane (**8**; 41.5 mg, 0.11 mmol) in 74% yield.

4,4,5,5-Tetramethyl-2-(3-(naphthalen-2-yl)-3-phenylpropyl)-1,3,2-dioxaborolane (8). Purified by GPC (chloroform): 41.5 mg (74%, 0.15 mmol scale); pale yellow solid; m.p. 74.3-75.3 °C; ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.78-7.73 (m, 2H), 7.71-7.69 (m, 2H), 7.44-7.36 (m, 2H), 7.33-7.30 (m, 1H), 7.28-7.22 (m, 4H), 7.16-7.12 (m, 1H), 3.99 (t, J = 7.7 Hz, 1H), 2.30-2.16 (m, 2H), 1.21 (s, 12H), 0.77 (t, J = 8.1 Hz, 2H). $^{13}C\{^{1}H\}$ NMR ($CDCl_3$, 100 MHz): δ 145.0, 142.5, 133.5, 132.1, 128.3, 128.2, 127.9, 127.7, 127.5, 127.0, 126.1, 126.0, 125.8, 125.2, 83.0, 53.7, 29.7, 24.8. (The carbon signal bound to boron was not observed due to quadrupolar relaxation.) ^{11}B NMR ($CDCl_3$, 128 MHz): δ 34.4. HRMS (APCI) m/z $(M)^+$ calcd for $C_{25}H_{29}BO_2$: 372.2260, found: 372.2235.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publication website at DOI: 10.1021/acs.joc.xxxx.

^{1}H, $^{13}C\{^{1}H\}$, $^{19}F\{^{1}H\}$, and ^{11}B NMR spectra for products, detailed optimization studies, and chiral HPLC charts (PDF)

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Notes

The authors declare no competing financial interest.

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