

Title	Palladium-Catalyzed Cross-Coupling Reaction of Diarylmethanol Derivatives with Diborylmethane
Author(s)	Asai, Kento; Miura, Masahiro; Hirano, Koji
Citation	Journal of Organic Chemistry. 2022, 87(11), p. 7436-7445
Version Type	AM
URL	https://hdl.handle.net/11094/92692
rights	© 2022 American Chemical Society.
Note	

Osaka University Knowledge Archive : OUKA

<https://ir.library.osaka-u.ac.jp/>

Osaka University

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

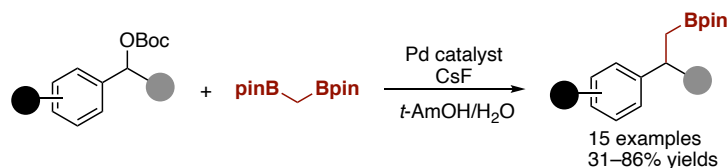
Kento Asai,[†] Masahiro Miura,[‡] and Koji Hirano^{†}*

[†]Department of Applied Chemistry, Graduate School of Engineering, Osaka University, Suita, Osaka 565-0871, Japan

[‡]Innovative Catalysis Science Division, Institute for Open and Transdisciplinary Research Initiatives (ICS-OTRI), Osaka University, Suita, Osaka 565-0871, Japan

RECEIVED DATE (to be automatically inserted after your manuscript is accepted if required according to the journal that you are submitting your paper to)

k_hirano@chem.eng.osaka-u.ac.jp

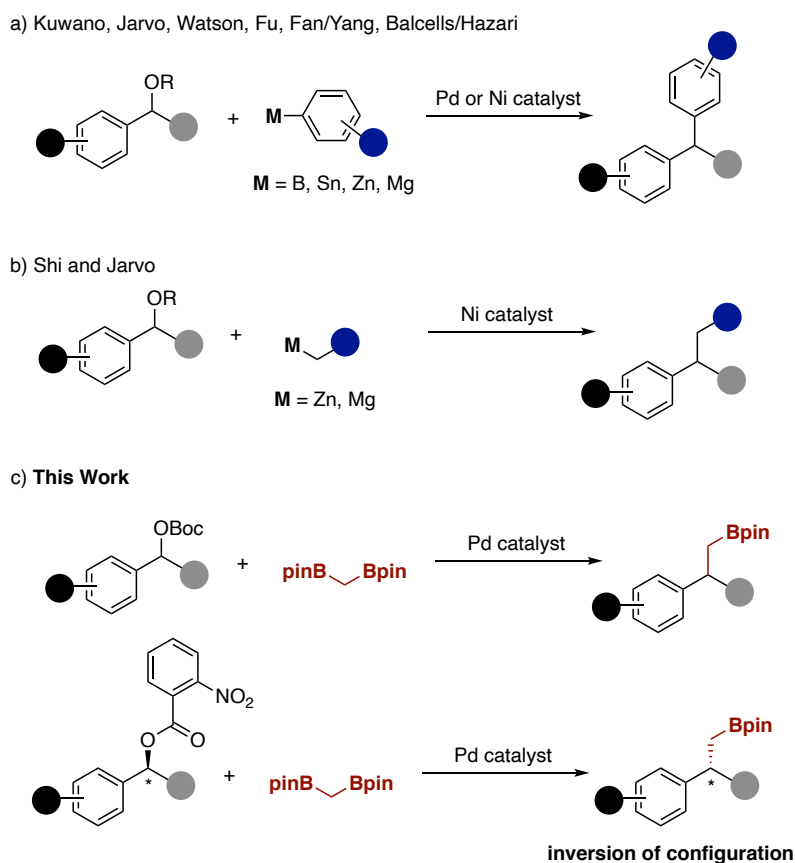


A palladium-catalyzed cross-coupling reaction of diarylmethanol derivatives with diborylmethane has been developed. The reaction proceeds chemoselectively to deliver the corresponding homobenzylic boronates in good yields.

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)

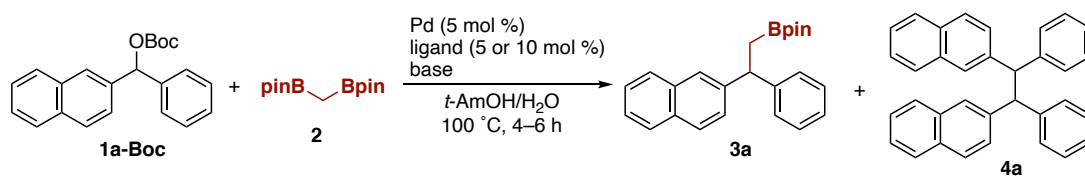


Results and Discussion

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(η^3 -C₃H₅)]₂/P[3,5-(*t*-Bu)₂-4-MeOC₆H₂]₃ catalyst and K₂CO₃ base in a *t*-AmOH/H₂O (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% ¹H 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-MeC₆H₄)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-MeC₆H₄)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-MeC₆H₄)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-(NO₂)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-(NO₂)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 H₂O 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**

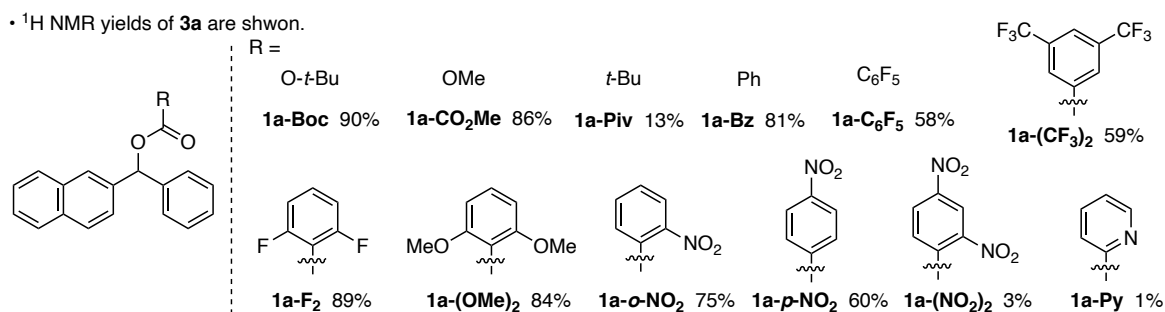


entry	Pd/ligand	base	yield (%) ^b	
			3a	4a
1	[PdCl(η^3 -C ₃ H ₅)] ₂ /P[3,5-(<i>t</i> -Bu) ₂ -4-MeOC ₆ H ₂] ₃	K ₂ CO ₃	16	5
2	[PdCl(η^3 -C ₃ H ₅)] ₂ /P[3,5-(<i>t</i> -Bu) ₂ C ₆ H ₃] ₃	K ₂ CO ₃	27	4
3	[PdCl(η^3 -C ₃ H ₅)] ₂ /P[3,5-(CF ₃) ₂ C ₆ H ₃] ₃	K ₂ CO ₃	0	trace
4	[PdCl(η^3 -C ₃ H ₅)] ₂ /PPh ₃	K ₂ CO ₃	56	24
5	[PdCl(η^3 -C ₃ H ₅)] ₂ /P(4-MeOC ₆ H ₄) ₃	K ₂ CO ₃	42	28
6	[PdCl(η^3 -C ₃ H ₅)] ₂ /P(4-MeC ₆ H ₄) ₃	K ₂ CO ₃	63	15
7	[PdCl(η^3 -C ₃ H ₅)] ₂ /P(4-FC ₆ H ₄) ₃	K ₂ CO ₃	12	5
8	[PdCl(η^3 -C ₃ H ₅)] ₂ /dppbz	K ₂ CO ₃	3	11
9	[PdCl(η^3 -C ₃ H ₅)] ₂ /dppe	K ₂ CO ₃	4	5
10	[PdCl(η^3 -C ₃ H ₅)] ₂ /dppp	K ₂ CO ₃	15	18
11	[PdCl(η^3 -C ₃ H ₅)] ₂ /dppb	K ₂ CO ₃	48	33
12	[PdCl(η^3 -C ₃ H ₅)] ₂ / <i>rac</i> -BINAP	K ₂ CO ₃	41	18
13	[PdCl(η^3 -C ₃ H ₅)] ₂ /dppf	K ₂ CO ₃	33	48
14	Pd[P(<i>t</i> -Bu) ₃] ₂ /none	K ₂ CO ₃	11	1
15	PEPPSI-IPr/none	K ₂ CO ₃	13	24
16	Pd(OAc) ₂ /P(4-MeC ₆ H ₄) ₃	K ₂ CO ₃	69	7
17	PdCl ₂ /P(4-MeC ₆ H ₄) ₃	K ₂ CO ₃	54	21
18	Pd ₂ (dba) ₃ /P(4-MeC ₆ H ₄) ₃	K ₂ CO ₃	38	10

19	CpPd(η^3 -C ₃ H ₅)/P(4-MeC ₆ H ₄) ₃	K ₂ CO ₃	43	10
20 ^c	Pd(OAc) ₂ /P(4-MeC ₆ H ₄) ₃	K ₂ CO ₃	84	5
21 ^c	Pd(OAc) ₂ /P(4-MeC ₆ H ₄) ₃	KF	74	6
22 ^c	Pd(OAc) ₂ /P(4-MeC ₆ H ₄) ₃	TBAF•3H ₂ O	11	44
23 ^c	Pd(OAc) ₂ /P(4-MeC ₆ H 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/H₂O (1.0/0.10 mL), 100 °C, 4–6 h, N₂. ^b Estimated by ¹H NMR with 1-methylnaphthalene as the internal standard. Isolated yield in parentheses. ^c With **2** (0.60 mmol).

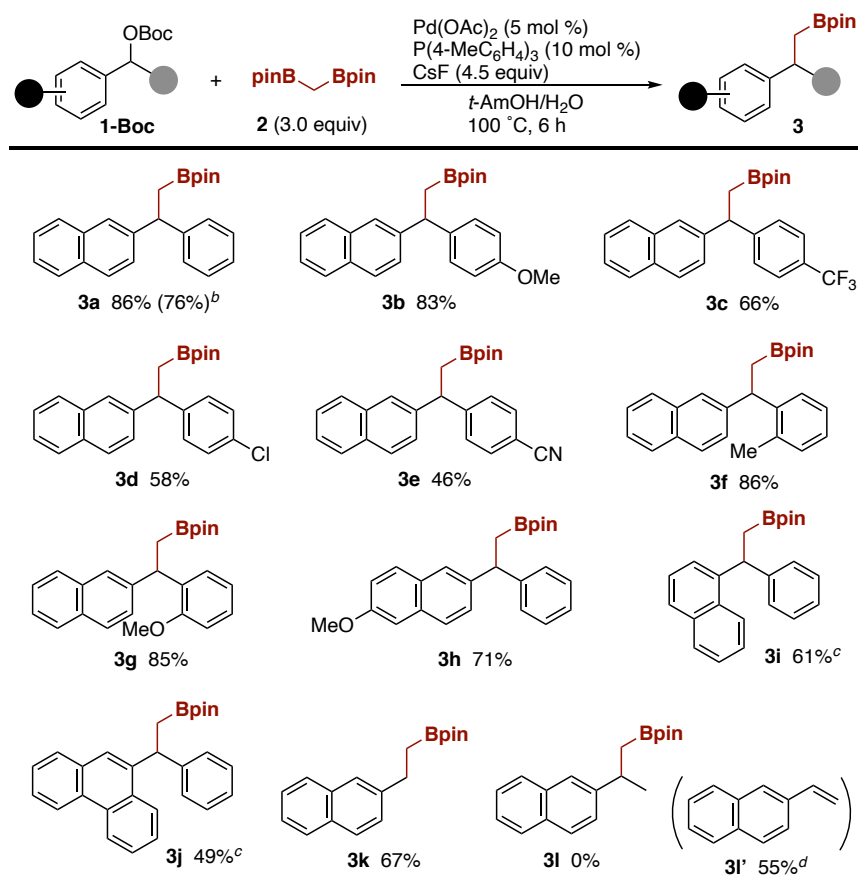
Scheme 2. Leaving Group Effects under Conditions of Entry 23 in Table 1



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

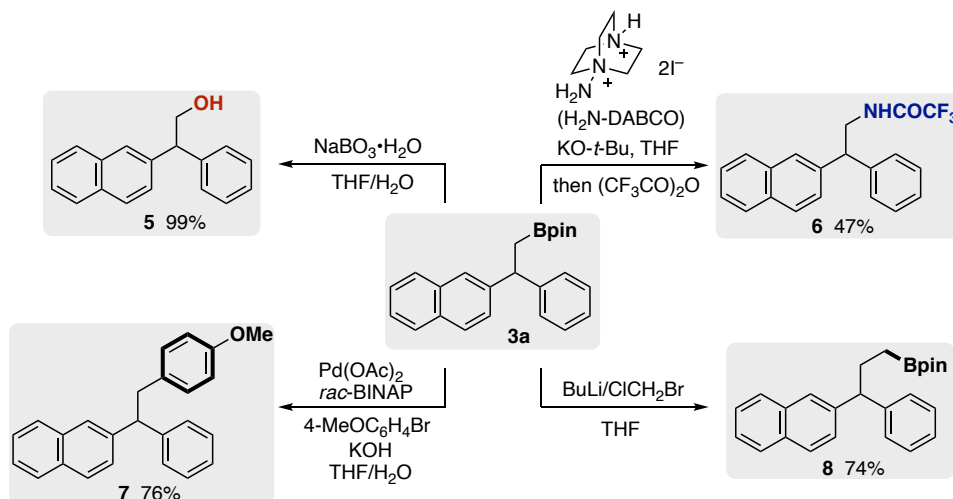


^a Conditions: **1-Boc** (0.20 mmol), **2** (0.30 mmol), Pd(OAc)₂ (0.010 mmol), P(4-MeC₆H₄)₃ (0.020 mmol), CsF (0.90 mmol), *t*-AmOH/H₂O (1.0/0.10 mL), 100 °C, 6 h, N₂. Isolated yields are shown. ^b On a 1.0 mmol scale. ^c At 120 °C. ^d Estimated by ¹H NMR in the crude mixture.

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 NaBO₃ and H₂N-DABCO,¹³ respectively. The Suzuki-Miyaura

cross-coupling with 4-bromoanisole was also feasible in the presence of $\text{Pd}(\text{OAc})_2/\text{rac-BINAP}$ catalyst¹⁴ 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 carbenoid¹⁵ proceeded smoothly to deliver the bis-homobenzylic pinacol boronate **8** in a good yield.

Scheme 4. Derivatizations of Bpin Moiety of **3a**^a

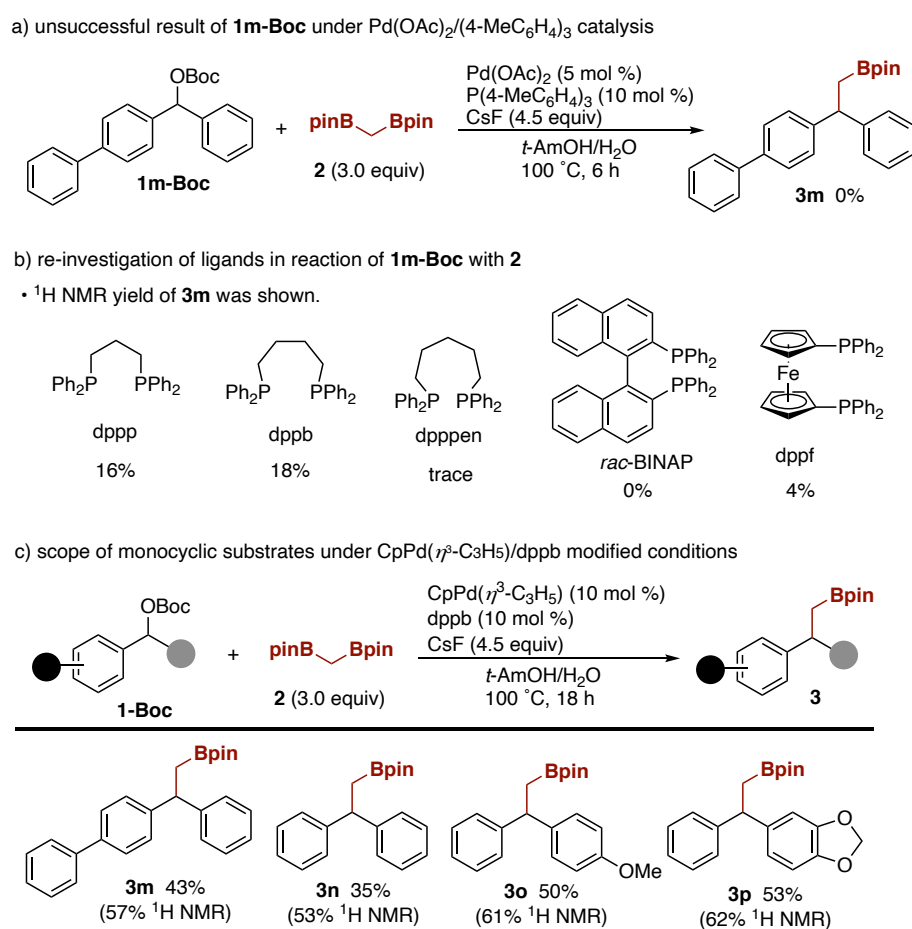


^a See the Experimental Section for detailed conditions of each procedure.

As mentioned in Scheme 3, several naphthalene-derived diarylmethyl carbonates were successfully cross-coupled with **2** under $\text{Pd}/\text{P}(4\text{-MeC}_6\text{H}_4)_3$ 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 $\text{CpPd}(\eta^3\text{-C}_3\text{H}_5)/\text{dppb}$ catalyst the targeted **3m** was formed with a synthetically acceptable level (57% ^1H NMR yield and 43% isolated yield; Scheme 5c). The modified catalyst system was uniquely effective¹⁷ 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

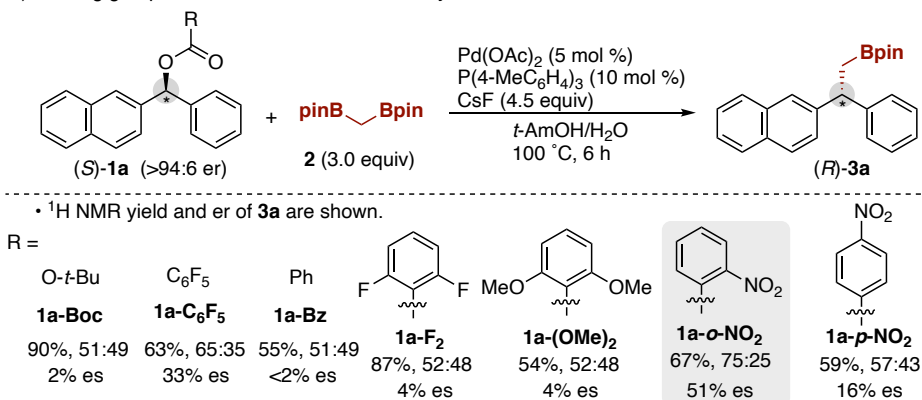


We finally attempted the enantiospecific cross-coupling reaction. When the independently prepared enantioenriched (*S*)-**1a-Boc**¹⁸ was subjected to the standard conditions with $\text{Pd}(\text{OAc})_2/\text{P}(4\text{-MeC}_6\text{H}_4)_3$ and CsF , the stereochemical information of the starting substrate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

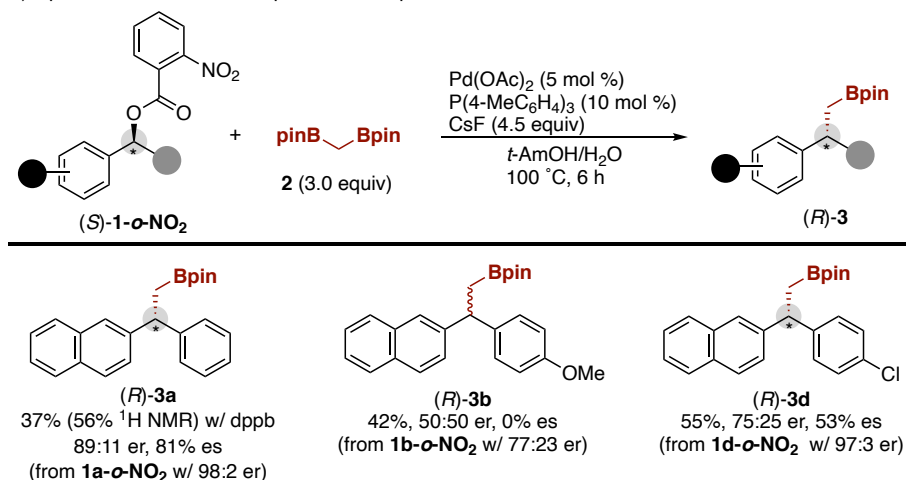
was formed as a racemate (Scheme 6a; **1a-Boc**, 2% es). On the other hand, moderate but meaningful stereochemical fidelity was observed from (*S*)-**1a-C₆F₅**: the stereoinvertive (*R*)-**3a** was obtained albeit with a 65:35 enantiomeric ratio. This phenomenon prompted us to further investigate the leaving group effect on the enantiospecificity. The simple benzoate (*S*)-**1a-Bz**, moderately electron-deficient (*S*)-**1a-F₂**, 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*-NO₂**. 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*-NO₂** 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*-NO₂**, in which the dppb ligand did not work well (only 4% ¹H NMR yield of **3d**; data not shown) and thus the standard conditions using P(4-MeC₆H₄)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

a) Leaving group effects in stereochemical fidelity



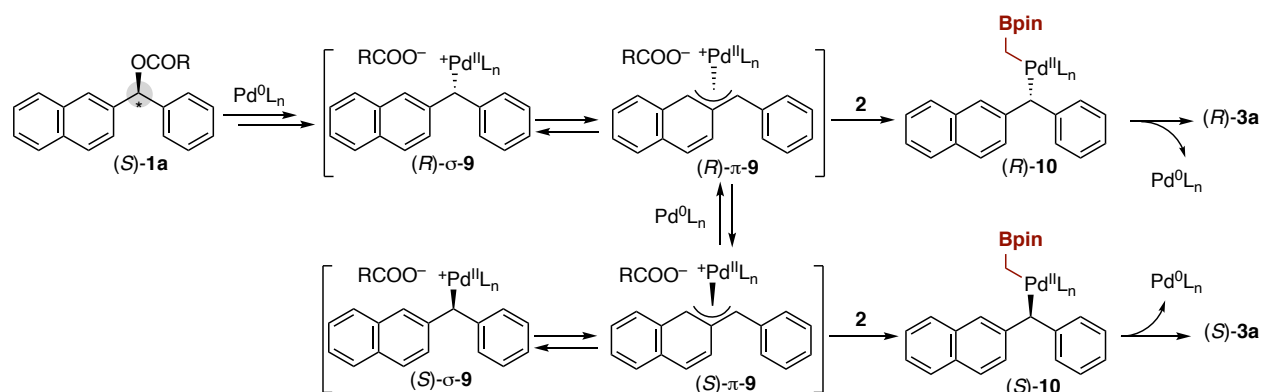
b) Optimal conditions and scope of enantiospecific reaction



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 Pd⁰L_n. The S_N2-type oxidative addition of Pd⁰L_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**.^{16c} 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 Pd⁰L_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**-F₂, and (*S*)-**1a**-(MeO)₂ are such cases. On the other hand, when (*S*)-**1a**-C₆F₅ or (*S*)-**1a**-*o*-NO₂ is employed, the transmetalation step

proceeds relatively smoothly because of the higher leaving ability of the corresponding weakly basic benzoate ion ($\text{RCOO}^- = \text{C}_6\text{F}_5\text{COO}^-$ or $o\text{-NO}_2\text{C}_6\text{H}_4\text{COO}^-$). 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 $\text{p}K_{\text{a}}$ value of the conjugate acid of the leaving group was not observed: for example, the $\text{p}K_{\text{a}}$ values of 2,6-(MeO)₂C₆H₃COOH and 4-NO₂C₆H₄COOH 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 ^1H , $^{13}\text{C}\{^1\text{H}\}$, $^{19}\text{F}\{^1\text{H}\}$, 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 chromatography analyses were performed on commercial glass plates bearing a 0.25 mm layer of Merck silica gel 60F₂₅₄. 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. $\text{CpPd}(\eta^3\text{-C}_3\text{H}_5)$ 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**.** $\text{Pd}(\text{OAc})_2$ (2.3 mg, 0.010 mmol, 5 mol %) and $\text{P}(4\text{-MeC}_6\text{H}_4)_3$ (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 ^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.

1.0 mmol Scale Synthesis of 3a. $\text{Pd}(\text{OAc})_2$ (11.2 mg, 0.050 mmol, 5 mol %) and $\text{P}(4\text{-MeC}_6\text{H}_4)_3$ (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 ^1H 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; ^1H 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). $^{13}\text{C}\{^1\text{H}\}$ 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 ($\text{M}+\text{H}$) $^+$ calcd for $\text{C}_{24}\text{H}_{28}\text{BO}_2$: 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; ^1H 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). $^{13}\text{C}\{^1\text{H}\}$ 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 $\text{C}_{25}\text{H}_{29}\text{BO}_3$: 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; ^1H 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). $^{13}\text{C}\{^1\text{H}\}$ 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. $^{19}\text{F}\{^1\text{H}\}$ NMR (CDCl_3 , 376 MHz): δ -62.30 (s). HRMS (APCI) m/z (M) $^+$ calcd for $\text{C}_{25}\text{H}_{26}\text{BF}_3\text{O}_2$: 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; ¹H NMR (CDCl₃, 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). ¹³C{¹H} NMR (CDCl₃, 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.) ¹¹B NMR (CDCl₃, 128 MHz): δ 33.9. HRMS (APCI) *m/z* (M)⁺ calcd for C₂₄H₂₆BClO₂: 392.1713, found: 392.1739.

4-(1-(Naphthalen-2-yl)-2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)ethyl)benzotrile (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; ¹H NMR (CDCl₃, 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). ¹³C{¹H} NMR (CDCl₃, 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.) ¹¹B NMR (CDCl₃, 128 MHz): δ 34.1. HRMS (APCI) *m/z* (M+H)⁺ calcd for C₂₅H₂₇BNO₂: 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; ¹H NMR (CDCl₃, 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).

$^{13}\text{C}\{^1\text{H}\}$ 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 $\text{C}_{25}\text{H}_{29}\text{BO}_2$: 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 $^\circ\text{C}$; ^1H 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). $^{13}\text{C}\{^1\text{H}\}$ 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 $\text{C}_{25}\text{H}_{29}\text{BO}_3$: 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 $^\circ\text{C}$; ^1H 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). $^{13}\text{C}\{^1\text{H}\}$ 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 ($\text{M}+\text{H}$) $^+$ calcd for $\text{C}_{25}\text{H}_{30}\text{BO}_3$: 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; ¹H NMR (CDCl₃, 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). ¹³C{¹H} NMR (CDCl₃, 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.) ¹¹B NMR (CDCl₃, 128 MHz): δ 34.2. HRMS (APCI) *m/z* (M)⁺ calcd for C₂₄H₂₇BO₂: 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; ¹H NMR (CDCl₃, 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). ¹³C{¹H} NMR (CDCl₃, 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.) ¹¹B NMR (CDCl₃, 128 MHz): δ 34.5. HRMS (APCI) *m/z* (M)⁺ calcd for C₂₈H₂₉BO₂: 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; ¹H NMR (CDCl₃, 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). $^{13}\text{C}\{^1\text{H}\}$ 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 $\text{C}_{18}\text{H}_{23}\text{BO}_2$: 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. $\text{CpPd}(\eta^3\text{-C}_3\text{H}_5)$ (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).

$^{13}\text{C}\{^1\text{H}\}$ 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 $\text{C}_{26}\text{H}_{29}\text{BO}_2$: 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; ^1H 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). $^{13}\text{C}\{^1\text{H}\}$ 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 ($\text{M}+\text{H}$) $^+$ calcd for $\text{C}_{20}\text{H}_{26}\text{BO}_2$: 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; ^1H 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). $^{13}\text{C}\{^1\text{H}\}$ 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 $\text{C}_{21}\text{H}_{27}\text{BO}_3$: 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; ^1H 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). $^{13}\text{C}\{^1\text{H}\}$ 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 $\text{C}_{21}\text{H}_{25}\text{BO}_4$: 352.1844, found: 352.1834.

General Procedure for the Pd-Catalyzed Enantiospecific Cross-Coupling Reaction of Diarylmethanol Derivatives 1 with Diborylmethane 2. $\text{Pd}(\text{OAc})_2$ (2.3 mg, 0.010 mmol, 5 mol %) and $\text{P}(4\text{-MeC}_6\text{H}_4)_3$ (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*-NO₂**; 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, $[\alpha]_{\text{D}}^{20} -5.31$ (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 $\text{NaBO}_3 \cdot \text{OH}_2$ (229.4 mg, 2.3 mmol) were placed in a 20 mL

round-bottom flask. Tetrahydrofuran (THF)/H₂O (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. Na₂S₂O₃ 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 °C; ¹H NMR (CDCl₃, 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). ¹³C{¹H} NMR (CDCl₃, 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 C₁₈H₁₆O: 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 NH₂-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 °C (oil bath). TFAA (42 μL, 0.30 mmol) was then added, and the reaction mixture was heated at 100 °C for additional 1 h (oil bath). The reaction was quenched with ethyl acetate and H₂O, 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; ¹H NMR (CDCl₃, 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). ¹³C{¹H} NMR (CDCl₃, 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. ¹⁹F{¹H} NMR (CDCl₃, 376 MHz): δ -76.00 (s). HRMS (APCI) *m/z* (M+H)⁺ calcd for C₂₀H₁₇F₃NO: 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. H₂O (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 ¹H NMR in CDCl₃ 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; ¹H NMR (CDCl₃, 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). $^{13}\text{C}\{^1\text{H}\}$ 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 $\text{C}_{25}\text{H}_{22}\text{O}$: 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 °C 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 °C 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; ^1H 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). $^{13}\text{C}\{^1\text{H}\}$ 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 $\text{C}_{25}\text{H}_{29}\text{BO}_2$: 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.xxxxx.

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

AUTHOR INFORMATION

Corresponding Author

Koji Hirano – *Department of Applied Chemistry, Graduate School of Engineering, Osaka University, Suita, Osaka 565-0871, Japan; orcid.org/0000-0001-9752-1985;*

Email: k_hirano@chem.eng.osaka-u.ac.jp.

Authors

Masahiro Miura – *Innovative Catalysis Science Division, Institute for Open and Transdisciplinary Research Initiatives (ICS-OTRI), Osaka University, Suita, Osaka 565-0871, Japan; orcid.org/0000-0001-8288-6439.*

Kento Asai – *Department of Applied Chemistry, Graduate School of Engineering, Osaka University, Suita, Osaka 565-0871, Japan*

Notes

The authors declare no competing financial interest.

ACKNOWLEDGMENTS

This work was supported by JSPS KAKENHI grant nos. JP 18K19078 (Grant-in-Aid for Challenging Research (Exploratory)) to K.H. and JP 17H06092 (Grant-in-Aid for Specially Promoted Research) to M.M.

References

- (1) (a) Metal-Catalyzed Cross-Coupling Reactions, 2nd ed. (Eds.: de Meijere, A.; Diederich, F.), Wiley-VCH, Weinheim, **2004**. (b) Tsuji, J. Palladium Reagents and Catalysts, 2nd ed., Wiley, Chichester, **2004**. (c) Cross-Coupling Reactions (*Top. Curr. Chem.* **219**, Ed.: Miyaura, N.), Springer, Berlin, **2002**. (d) Suzuki, A. Cross-Coupling Reactions Of Organoboranes: An Easy Way To Construct C–C Bonds (Nobel Lecture). *Angew. Chem., Int. Ed.* **2011**, *50*, 6723–6737. (e) Negishi, E.-i. Magical Power of Transition Metals: Past, Present, and Future (Nobel Lecture). *Angew. Chem., Int. Ed.* **2011**, *50*, 6738–6764.
- (2) Selected reviews and accounts: (a) Yu, D.-G.; Li, B.-J.; Shi, Z.-J. Exploration of New C–O Electrophiles in Cross-Coupling Reactions. *Acc. Chem. Res.* **2010**, *43*, 1486–1495. (b) Mesganaw, T.; Garg, N. K. Ni- and Fe-Catalyzed Cross-Coupling Reactions of Phenol Derivatives. *Org. Process Res. Dev.* **2013**, *17*, 29–39. (c) Cornella, J.; Zarate, C.; Martin, R. Metal-catalyzed activation of ethers via C–O bond cleavage: a new strategy for molecular diversity. *Chem. Soc. Rev.* **2014**, *43*, 8081–8097. (d) Tobisu, M.; Chatani, N. Cross-Couplings Using Aryl Ethers via C–O Bond Activation Enabled by Nickel Catalysts. *Acc. Chem. Res.* **2015**, *48*, 1717–1726. (e) Qiu, Z.; Li, C.-J. Transformations of Less-Activated Phenols and Phenol Derivatives via C–O Cleavage. *Chem. Rev.* **2020**, *120*, 10454–10515.
- (3) (a) Kuwano, R.; Yokogi, M. Suzuki–Miyaura Cross-Coupling of Benzylic Carbonates with Arylboronic Acids. *Org. Lett.* **2005**, *7*, 945–947. (b) Yu, J.-Y.; Kuwano, R. Suzuki-Miyaura Coupling of Diarylmethyl Carbonates with Arylboronic Acids: A New Access to Triarylmethanes. *Org. Lett.* **2008**, *10*, 973–976. (c) Ohsumi, M.; Kuwano, R. Palladium-catalyzed Cross-coupling of Benzylic Carbonates with Organostannanes. *Chem. Lett.* **2008**, *37*, 796–797.
- (4) (a) Taylor, B. L. H.; Harris, M. R.; Jarvo, E. R. Synthesis of Enantioenriched Triarylmethanes by Stereospecific Cross-Coupling Reactions. *Angew. Chem., Int. Ed.* **2012**, *51*, 7790–7793. (b) Harris, M. R.; Hanna, L. E.; Gree, M. A.; Moore, C. E.; Jarvo, E. R. Retention or Inversion in Stereospecific Nickel-

Catalyzed Cross-Coupling of Benzylic Carbamates with Arylboronic Esters: Control of Absolute Stereochemistry with an Achiral Catalyst. *J. Am. Chem. Soc.* **2013**, *135*, 3303–3306.

(5) (a) Zhou, Q.; Srinivas, H. D.; Dasgupta, S.; Watson, M. P. Nickel-Catalyzed Cross-Couplings of Benzylic Pivalates with Arylboroxines: Stereospecific Formation of Diarylalkanes and Triarylmethanes. *J. Am. Chem. Soc.* **2013**, *135*, 3307–3310. (b) Zhou, Q.; Cobb, K. M.; Tan, T.; Watson, M. P. Stereospecific Cross Couplings To Set Benzylic, All-Carbon Quaternary Stereocenters in High Enantiopurity. *J. Am. Chem. Soc.* **2016**, *138*, 12057–12060. (c) Xu, J.; Bercher, O. P.; Watson, M. P. Overcoming the Naphthyl Requirement in Stereospecific Cross-Couplings to Form Quaternary Stereocenters. *J. Am. Chem. Soc.* **2021**, *143*, 8608–8613.

(6) Do, H.-Q.; Chandrashekar, E. R. R.; Fu, G. C. Nickel/Bis(oxazoline)-Catalyzed Asymmetric Negishi Arylations of Racemic Secondary Benzylic Electrophiles to Generate Enantioenriched 1,1-Diarylalkanes. *J. Am. Chem. Soc.* **2013**, *135*, 16288–16291.

(7) Chen, Q.; Fan, X.-H.; Zhang, L.-P.; Yang, L.-M. Ni(II) source as a pre-catalyst for the cross-coupling of benzylic pivalates with arylboronic acids: facile access to tri- and diarylmethanes. *RSC Adv.* **2015**, *5*, 15338–15340.

(8) Dardir, A. D.; Casademont-Reig, I.; Balcells, D.; Ellefsen, J. D.; Espinosa, M. R.; Hazari, N.; Smith, N. E. Synthesis of Triarylmethanes via Palladium-Catalyzed Suzuki–Miyaura Reactions of Diarylmethyl Esters. *Organometallics* **2021**, *40*, 2332–2344.

(9) (a) Guan, B.-T.; Xiang, S.-K.; Wang, B.-Q.; Sun, Z.-P.; Wang, Y.; Zhao, K.-Q.; Shi, Z.-J. Direct Benzylic Alkylation via Ni-Catalyzed Selective Benzylic sp³ C–O Activation. *J. Am. Chem. Soc.* **2008**, *130*, 3268–3269. (b) Taylor, B. L. H.; Swift, E. C.; Waetzig, J. D.; Jarvo, E. R. Stereospecific Nickel-Catalyzed Cross-Coupling Reactions of Alkyl Ethers: Enantioselective Synthesis of Diarylethanes. *J. Am. Chem. Soc.* **2011**, *133*, 389–391. (c) Greene, M. A.; Yonova, I. M.; Williams, F. J.; Jarvo, E. R. Traceless Directing Group for Stereospecific Nickel-Catalyzed Alkyl–Alkyl Cross-Coupling Reactions. *Org. Lett.* **2012**, *14*, 4293–4296. (d) Wisniewska, H. M.; Swift, E. C.; Jarvo, E. R. Functional-Group-Tolerant, Nickel-Catalyzed Cross-Coupling Reaction for Enantioselective Construction of Tertiary Methyl-Bearing

Stereocenters. *J. Am. Chem. Soc.* **2013**, *135*, 9083–9090. (e) Yonova, I. M.; Johnson, A. G.; Osborne, C. A.; Moore, C. E.; Morrisette, N. S.; Jarvo, E. R. Stereospecific Nickel-Catalyzed Cross-Coupling Reactions of Alkyl Grignard Reagents and Identification of Selective Anti-Breast-Cancer Agents. *Angew. Chem., Int. Ed.* **2014**, *53*, 2422–2427. (f) Tollefson, E. J.; Dawson, D. D.; Osborne, C. A.; Jarvo, E. R. Stereospecific Cross-Coupling Reactions of Aryl-Substituted Tetrahydrofurans, Tetrahydropyrans, and Lactones. *J. Am. Chem. Soc.* **2014**, *136*, 14951–14958.

(10) For pioneering work on the Pd-catalyzed cross-coupling with diborylmethanes, see: (a) Endo, K.; Ohkubo, T.; Hirokami, M.; Shibata, T. Chemoselective and Regiospecific Suzuki Coupling on a Multisubstituted sp^3 -Carbon in 1,1-Diborylalkanes at Room Temperature. *J. Am. Chem. Soc.* **2010**, *132*, 11033–11035. A recent review: (b) Nallagonda, R.; Padala, K.; Masarwa, A. *gem*-Diborylalkanes: recent advances in their preparation, transformation and application. *Org. Biomol. Chem.* **2018**, *16*, 1050–1064.

(11) Endo/Shibata and Morken independently reported the benzylation reaction of diborylalkanes under Pd-catalyzed and NaO-*t*-Bu-mediated conditions, respectively, but the benzylic electrophile was limited to the primary benzyl halide. (a) Endo, K.; Ohkubo, T.; Ishioka, T.; Shibata, T. Cross Coupling between sp^3 -Carbon and sp^3 -Carbon Using a Diboryl methane Derivative at Room Temperature. *J. Org. Chem.* **2012**, *77*, 4826–4831. (b) Hong, K.; Liu, X.; Morken, J. P. Simple Access to Elusive α -Boryl Carbanions and Their Alkylation: An Umpolung Construction for Organic Synthesis. *J. Am. Chem. Soc.* **2014**, *136*, 10581–10584.

(12) (a) Mukai, T.; Hirano, K.; Satoh, T.; Miura, M. Palladium-Catalyzed Direct Benzylation of Azoles with Benzyl Carbonates. *Org. Lett.* **2010**, *12*, 1360–1363. (b) Tabuchi, S.; Hirano, K.; Satoh, T.; Miura, M. Synthesis of Triarylmethanes by Palladium-Catalyzed C-H/C-O Coupling of Oxazoles and Diarylmethanol Derivatives. *J. Org. Chem.* **2014**, *79*, 5401–5411. (c) Tabuchi, S.; Hirano, K.; Miura, M. Stereospecific Pd-Catalyzed Intermolecular $C(sp^3)$ - $C(sp)$ Cross-Coupling of Diarylmethyl Carbonates and Terminal Alkynes Under Base-Free Conditions. *Chem.–Eur. J.* **2015**, *21*, 16823–16827. (d) Tabuchi, S.; Hirano, K.; Miura, M. Palladium-Catalyzed Asymmetric Benzylic Alkylation of Active Methylene

Compounds with α -Naphthylbenzyl Carbonates and Pivalates. *Angew. Chem., Int. Ed.* **2016**, *55*, 6973–6977. (e) Najib, A.; Hirano, K.; Miura, M. Palladium-Catalyzed Asymmetric Benzylic Substitution of Secondary Benzyl Carbonates with Nitrogen and Oxygen Nucleophiles. *Org. Lett.* **2017**, *19*, 2438–2441. (f) Najib, A.; Hirano, K.; Miura, M. Asymmetric Synthesis of Diarylmethyl Sulfones by Palladium-Catalyzed Enantioselective Benzylic Substitution: A Remarkable Effect of Water. *Chem.–Eur. J.* **2018**, *24*, 6525–6529. (g) Matsude, A.; Hirano, K.; Miura, M. Palladium-Catalyzed Benzylic Phosphorylation of Diarylmethyl Carbonates. *Org. Lett.* **2018**, *20*, 3553–3556. (h) Asai, K.; Hirano, K.; Miura, M. Divergent Synthesis of Isonitriles and Nitriles by Palladium-Catalyzed Benzylic Substitution with TMSCN. *J. Org. Chem.* **2020**, *85*, 12703–12714. (i) Asai, K.; Hirano, K.; Miura, M. Palladium-Catalyzed Benzylic Silylation of Diarylmethyl Carbonates with Silylboranes under Base-Free Conditions. *Eur. J. Org. Chem.* **2022**, *22*, No. e202101535. (j) Matsude, A.; Hirano, K.; Miura, M. Highly Stereoselective Synthesis of 1,2-Disubstituted Indanes by Pd-Catalyzed Heck/Suzuki Sequence of Diarylmethyl Carbonates. *Org. Lett.* **2020**, *22*, 3190–3194.

(13) Liu, X.; Zhu, Q.; Chen, D.; Wang, L.; Jin, L.; Liu, C. Aminoazanium of DABCO: An Amination Reagent for Alkyl and Aryl Pinacol Boronates. *Angew. Chem., Int. Ed.* **2020**, *59*, 2745–2749.

(14) Chen, B.; Cao, P.; Yin, X.; Liao, Y.; Jiang, L.; Ye, J.; Wang, M.; Liao, J. Modular Synthesis of Enantioenriched 1,1,2-Triarylethanes by an Enantioselective Arylboration and Cross-Coupling Sequence. *ACS Catal.* **2017**, *7*, 2425–2429.

(15) (a) Brown, H. C.; Singh, S. M.; Rangaishevi, M. V. Organoboranes. 46. New procedures for the homologation of boronic esters. A critical examination of the available procedures to achieve convenient homologation of boronic esters. *J. Org. Chem.* **1986**, *51*, 3150–3155. (b) Matteson, D. S. α -Halo boronic esters: intermediates for stereodirected synthesis. *Chem. Rev.* **1989**, *89*, 1535–1551.

(16) (a) Tollefson, E. J.; Hanna, L. E.; Jarvo, E. R. Stereospecific Nickel-Catalyzed Cross-Coupling Reactions of Benzylic Ethers and Esters. *Acc. Chem. Res.* **2015**, *48*, 2344–2353. (b) Muto, K.; Yamaguchi, J.; Itami, K. Nickel-Catalyzed C–H/C–O Coupling of Azoles with Phenol Derivatives. *J. Am. Chem. Soc.*

2012, *134*, 169–172. (c) Mendis, S. M.; Tunge, J. A. Palladium-Catalyzed Stereospecific Decarboxylative Benzoylation of Alkynes. *Org. Lett.* **2015**, *17*, 5164–5167. (d) Correa, A.; Martin, R. Ni-Catalyzed Direct Reductive Amidation via C–O Bond Cleavage. *J. Am. Chem. Soc.* **2014**, *136*, 7523–7526. Also see, ref 2. Such a specific reactivity of π -extended naphthalene-type derivatives can be associated with their lower aromaticity, compared to the simple phenyl derivatives. (e) Trost, B. M.; Czabaniuk, L. C. Structure and Reactivity of Late Transition Metal η^3 -Benzyl Complexes. *Angew. Chem., Int. Ed.* **2014**, *53*, 2826–2851. (f) Le Bras, J. L.; Muzart, J. Production of Csp³–Csp³ Bonds through Palladium-Catalyzed Tsuji–Trost-Type Reactions of (Hetero)Benzylic Substrates. *Eur. J. Org. Chem.* **2016**, *2016*, 2565–2593.

(17) The CpPd(η^3 -C₃H₅)/dppb-modified catalyst was not effective for the naphthalene-type substrate. For instance, **1a-Boc** provided **3a** in only 22% ¹H NMR yield, and the major product was homocoupled **4a** (44% ¹H NMR yield).

(18) Braga, A. L.; Paixão, M. W.; Westermann, B.; Schneider, P. H.; Wessjohann, L. A. Acceleration of Arylzinc Formation and Its Enantioselective Addition to Aldehydes by Microwave Irradiation and Aziridine-2-methanol Catalysts. *J. Org. Chem.* **2008**, *73*, 2879–2882.

(19) In the case of MeO-substituted substrate **1b-o-NO₂**, we cannot exclude the possibility that racemization occurs via a free benzyl cation intermediate.

(20) For precedents of S_N2-type oxidative addition of alkyl electrophiles to Pd⁰, see: (a) Wong, P. K.; Lau, K. S. Y.; Stille, J. K. Stereochemistry of oxidative addition of benzyl- α -d chloride to tetrakis(triphenylphosphine)palladium(0). Direct evidence for configurational inversion at carbon via a nonradical mechanism. *J. Am. Chem. Soc.* **1974**, *96*, 5956–5957. (b) Hills, I. D.; Netherton, M. R.; Fu, G. C. Toward an Improved Understanding of the Unusual Reactivity of Pd⁰/Trialkylphosphane Catalysts in Cross-Couplings of Alkyl Electrophiles: Quantifying the Factors That Determine the Rate of Oxidative Addition. *Angew. Chem., Int. Ed.* **2003**, *42*, 5749–5752. (c) López-Pérez, A.; Adrio, J.; Carretero, J. C. Palladium-Catalyzed Cross-Coupling Reaction of Secondary Benzylic Bromides with Grignard Reagents. *Org. Lett.* **2009**, *11*, 5514–5517. (d) Trost, B. M.; Czabaniuk, L. C. Benzylic Phosphates as Electrophiles

in the Palladium-Catalyzed Asymmetric Benzylolation of Azlactones. *J. Am. Chem. Soc.* **2012**, *134*, 5778–5781.

(21) For the related racemization process under nickel catalysis, see ref 9e. A similar mechanism was proposed in related π -allylpalladium chemistry: (a) Takahashi, T.; Jinbo, Y.; Kitamura, K.; Tsuji, J. Chirality transfer from C-O to C-C in the palladium catalyzed ScN' reaction of (E)- and (Z)-allylic carbonates with carbonucleophile. *Tetrahedron Lett.* **1984**, *25*, 5921–5924. (b) Granberg, K. L.; Bäckvall, J.-E. Isomerization of (π -allyl)palladium complexes via nucleophilic displacement by palladium(0). A common mechanism in palladium(0)-catalyzed allylic substitution. *J. Am. Chem. Soc.* **1992**, *114*, 6858–6863. (c) Moreno-Mañas, M.; Morral, L.; Pleixats, R. Palladium(0)-Catalyzed Allylation of Highly Acidic and Nonnucleophilic Anilines. The Origin of Stereochemical Scrambling When Using Allylic Carbonates. *J. Org. Chem.* **1998**, *63*, 6160–6166. (d) Ogoshi, S.; Kurosawa, H. Redox transmetalation reaction involving η^3 -allyl group transfer from palladium(II) to platinum(0). *Organometallics* **1993**, *12*, 2869–2871.

(22) For the related positive counter ion effect of weakly coordinating $^-\text{BAR}^{\text{F}_4}$ in the isoelectronic Pd-catalyzed allylic substitution reaction, see: Evans, L. A.; Fey, N.; Harvey, J. N.; Hose, D.; Lloyd-Jones, G. C.; Murray, P.; Orpen, A. G.; Osborne, R.; Owen-Smith, G. J. J.; Purdie, M. Counterintuitive Kinetics in Tsuji-Trost Allylation: Ion-Pair Partitioning and Implications for Asymmetric Catalysis. *J. Am. Chem. Soc.* **2008**, *130*, 14471–14473.

(23) For the $\text{p}K_{\text{a}}$ values, see: Harding, A. P.; Wedge, D. C.; Popelier, P. L. A. $\text{p}K_{\text{a}}$ Prediction from “Quantum Chemical Topology” Descriptors. *J. Chem. Inf. Model.* **2009**, *49*, 1914–1924. To increase the enantiospecificity, we also tried the preparation of the optically active diarylmethyl trifluoroacetate with CF_3COO^- of higher leaving ability from the enantioenriched diarylmethanol and $(\text{CF}_3\text{CO})_2\text{O}$. However, the corresponding trifluoroacetate was obtained in a racemic form, thus suggesting the facile racemization in the esterification step.

(24) We also tried the substituted diborylmethane, but the reaction remained unsuccessful. Only the reduced byproduct was formed probably via the predominant β -H elimination from an alkylpalladium intermediate. Additionally, attempts to apply asymmetric catalysis also remained unsuccessful. See the Supporting Information for details.

(25) Tatsuno, Y.; Yoshida, T.; Otsuka, S.; Al-Salem, N.; Shaw, B. L. (η^3 -Allyl)Palladium(II) Complexes. *Inorg. Synth.* **1990**, *28*, 342–345.