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Substrate switchable Suzuki–Miyaura coupling for benzyl ester vs. benzyl halide†

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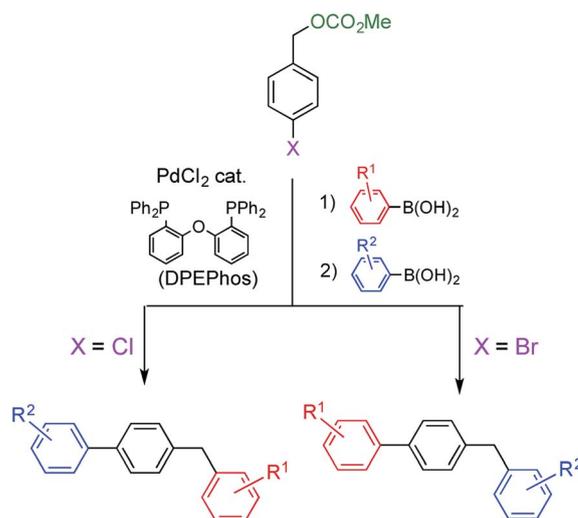
Two reaction conditions were developed to accomplish the substrate switchable Suzuki–Miyaura coupling of benzyl derivatives and arylboronic acid derivatives. Under conditions for esters, benzyl esters such as carbonates and acetates reacted with arylboronic acids to afford the corresponding diarylmethanes. However, the benzyl halides did not react under the same conditions. On the other hand, benzyl halides such as bromides and chlorides furnished diarylmethanes under conditions for halides, under which benzyl ester substrates did not react, in which water was found to play an important role. This switching system was tested using the intermolecular/intramolecular competitive reactions, during which the desired products could be synthesized by selecting the appropriate reaction conditions.

Introduction

Diarylmethanes are an important class of compounds because they are widely used as a framework for functional materials including polymers,¹ dyes,² and biologically active compounds.³ Various methods have been reported for their synthesis, including the Suzuki–Miyaura coupling reaction, which has become our focus.^{4–6} In a typical Suzuki–Miyaura coupling, benzyl esters (carbonates or acetates) are reacted with arylboronic acids in the presence of a Pd catalyst under air atmosphere to efficiently afford the corresponding diarylmethanes.⁵ In our protocol, the Pd catalyst is prepared from inexpensive and commercially available PdCl₂ and bidentate bis(phosphine) ligands. The ability to use an accessible catalyst improved the practicality of the reaction. Moreover, the reactivity of the benzyl esters was found to be between that of chloro- and bromobenzenes. This property facilitated the selective synthesis of benzyl(biphenyl)s by successive Suzuki–Miyaura coupling reactions (Scheme 1). These results prompted us to investigate a more challenging project; controlling chemoselectivity for benzyl esters and benzyl halides. In this study, we managed to successfully switch the substrate favored for coupling by changing the reaction conditions.

Results and discussion

When benzyl carbonate **1A** was reacted with phenylboronic acid (**5a**) (1.25 equiv.) in the presence of the Pd catalyst derived from PdCl₂ (5 mol%) and DPEPhos (5.5 mol%) in ethanol, the coupling reaction proceeded to afford diarylmethane **6Aa**^{4f} in a 76% yield after heating at 80 °C for 1 d (Table 1, entry 1). These conditions are referred to as conditions for esters, in which lack of any reagent did not undergo the reaction at all. Although benzyl acetate **2A** reacted similarly, its reactivity was lower than that of carbonate **1A** (entry 2). On the other hand, benzyl halides **3A** and **4A** did not react under the same conditions (entries 3 and 4). After surveying several reaction condition options, the choice of ligand, base, and solvent was found to be crucial to



Scheme 1 Chemoselective synthesis of benzyl(biphenyl)s.

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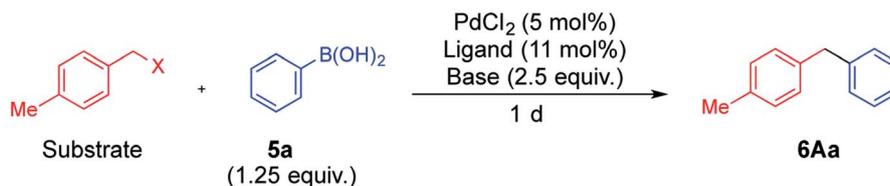
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† Electronic supplementary information (ESI) available: Experimental data for optimization of the reaction conditions, for chemoselective coupling reactions using other substrates; copies of ¹H and ¹³C NMR spectra. See DOI: 10.1039/c8ra07841f



Table 1 Assessment of switchable reaction conditions depending on the substrate



Entry	Substrate		Ligand	Base	Solv.	Temp./°C	Conversion of substrate/%	Yield ^a /%
	X							
1	OCOOMe	1A	DPEPhos	NaHCO ₃	EtOH	80	89	76
2	OAc	2A	DPEPhos	NaHCO ₃	EtOH	80	65	59
3	Br	3A	DPEPhos	NaHCO ₃	EtOH	80	6	0
4	Cl	4A	DPEPhos	NaHCO ₃	EtOH	80	4	0
5	Cl	4A	PPh ₃	Na ₂ CO ₃	EtOH	80	13	10
6	OCOOMe	1A	PPh ₃	Na ₂ CO ₃	THF/H ₂ O ^b	80	100	23
7	Cl	4A	PPh ₃	Na ₂ CO ₃	THF/H ₂ O ^b	80	100	92
8	Br	3A	PPh ₃	Na ₂ CO ₃	THF/H ₂ O ^b	80	100	89
9	OCOOMe	1A	PPh ₃	Na ₂ CO ₃	THF/H ₂ O ^b	40	4	0
10	Cl	4A	PPh ₃	Na ₂ CO ₃	THF/H ₂ O ^b	40	85	81
11	OCOOMe	1A	PPh ₃	Na ₂ CO ₃	THF/H ₂ O ^c	40	0	0
12	Cl	4A	PPh ₃	Na ₂ CO ₃	THF/H ₂ O ^c	40	78	74
13	OCOOMe	1A	PPh ₃	Na ₂ CO ₃	THF/EtOH ^b	40	8	4
14	Cl	4A	PPh ₃	Na ₂ CO ₃	THF/EtOH ^b	40	16	12
15	OCOOMe	1A	PPh ₃	Na ₂ CO ₃	THF	40	0	0
16	Cl	4A	PPh ₃	Na ₂ CO ₃	THF	40	9	4
17	Cl	4A	PPh ₃	Et ₃ N	THF	40	30	14
18	OCOOMe	1A	PPh ₃	Na ₂ CO ₃	PhMe/H ₂ O ^b	40	0	0
19	Cl	4A	PPh ₃	Na ₂ CO ₃	PhMe/H ₂ O ^b	40	67	62

^a Determined by ¹H NMR. ^b v/v = 1/1 (heterogeneous). ^c v/v = 4/1 (homogeneous).

switching the reactivity (Table S1 in the ESI[†]). A combination of triphenylphosphine and Na₂CO₃ facilitated the reaction of benzyl chloride **4A** (entry 5). A complete switch was made to afford **6Aa** efficiently while **1A** did not react (entries 6–10; successful reactions were performed in a mixed THF/water (v/v = 1/1) solvent at 40 °C, referred to conditions for halides). Benzyl bromide **3A** showed similar behavior to **4A** to undergo the coupling reaction efficiently only under conditions for halides (entry 8). Usually, THF and water is miscible; however, a mixed solvent (v/v = 1/1) was separated into two layers in this reaction. On the other hand, the yields of **6Aa** were considerably lower in reactions performed using a homogeneous mixed solvent of THF and water (v/v = 4/1), THF and ethanol (v/v = 1/1) or THF alone (entries 11–16). In addition, triethylamine was not an effective base for this reaction (entry 17). To the contrary, the reaction proceeded more efficiently when a mixed solvent of toluene and water (v/v = 1/1) was employed (entries 18 and 19). Based on these results, the presence of water was found to be crucial for this reaction. Although there is a report that aqueous conditions are effective for the reaction using DPEPhos, exact role of water was not mentioned.⁷

In order to obtain insights for the role of water, density functional theory (DFT) calculation using B3LYP was performed for two plausible intermediate complexes [PdBnCl(PPh₃)₂] (+H₂O) and [PdBnCl(PPh₃)(OH₂)] (+PPh₃) (Table 2, Fig. 1 and 2).

By comparing the ΔG_{tot} values of these complexes, the latter is thermodynamically favored by −ΔG_{tot} = 0.032521 a.u. (20.4 kcal mol^{−1}).

It is considered that different reactivity between benzyl esters and benzyl halides are brought about different mode during the oxidative addition steps in the catalytic cycle. When benzyl carbonate **1A** undergoes oxidative addition to Pd⁰ species, π-complex **7** is formed accompanied by decarboxylation (Scheme 2, eqn (1)). Benzyl acetate **2A** also affords similar complex intermediately. On the other hand, in cases of benzyl chloride **4A**, σ-complex **8** is formed, and benzyl bromide **3A** also affords similar complex. One of the phosphine ligands in **8** is easily exchanged with water leading to complex **9**, which undergoes the subsequent coupling reaction efficiently (eqn (2)).

Other benzyl derivatives **1–4** were coupled under the conditions optimized for 4-methylbenzyl carbonate **1A** (conditions for esters) or 4-methylbenzyl chloride **4A** (conditions for halides), and each reaction proceeded in high conversion yield (Table 3). Under conditions for esters, benzyl carbonates **1** and benzyl acetates **2** exhibited similar reactivity to afford the corresponding diarylmethanes **6** in comparable yields; however, benzyl halides **3** and **4** did not react except for highly reactive methoxy derivatives **3B** and **4B** (Table S2 in ESI[†]). To the contrary, only benzyl halides **3** and **4** coupled under conditions for halides, and no reaction was observed when benzyl esters **1**



Table 2 Thermodynamic parameters of [PdBnCl(PPh₃)L]

Compound	E_0^a /a.u.	G_{corr}^a /a.u.	G_{tot}^a /a.u.
[PdBnCl(PPh ₃)(OH ₂)]	-1970.727043	+0.356655	-1970.370388
PPh ₃	-1036.322130	+0.227447	-1036.094683
[Pd(Bz)Cl(PPh ₃)(OH ₂)] (+PPh ₃)			-3006.465071
[PdBnCl(PPh ₃) ₂]	-2930.603622	+0.587757	-2930.015865
H ₂ O	-76.419737	+0.003052	-76.416685
[PdBnCl(PPh ₃) ₂] (+H ₂ O)			-3006.432550

^a E_0 : total electronic energy, G_{corr} : thermal correction to Gibbs free energy, G_{tot} : sum of electronic and thermal free energies.

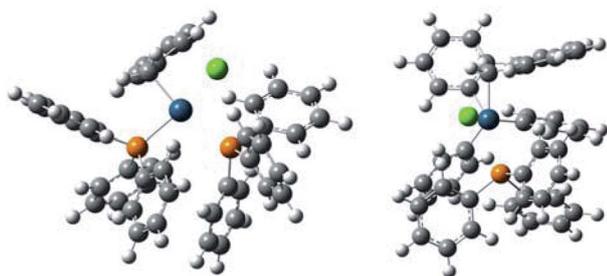


Fig. 1 Optimized geometry of [PdBnCl(PPh₃)₂]: top view (left) and side view (right).

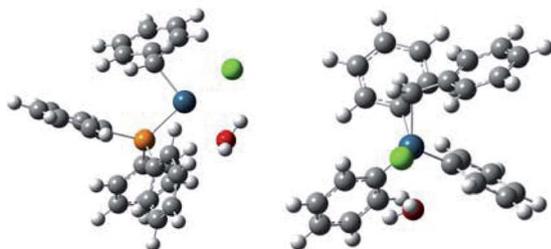
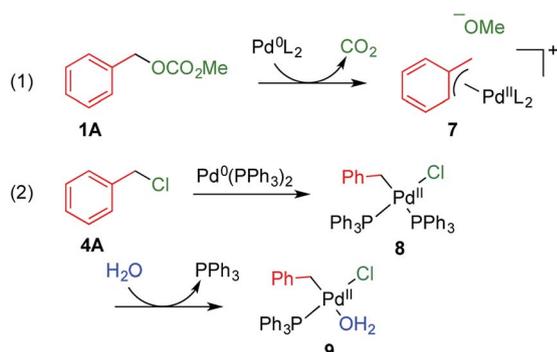


Fig. 2 Optimized geometry of [PdBnCl(PPh₃)(OH₂)]: top view (left) and side view (right).

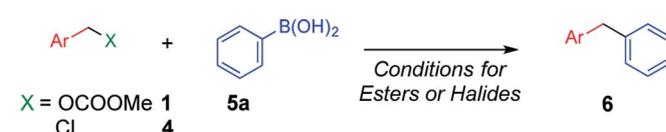


Scheme 2 Plausible intermediate complexes in the coupling reactions using benzyl carbonate **1A** and benzyl chloride **4A**.

and **2** were employed (Table S3 in ESI[†]). In cases of the less reactive, electron-deficient benzyl chlorides **4C–F**, yields of diarylmethanes **6Ca–Fa** were higher than those obtained in the reactions using **1C–F** under conditions for esters.

When other boronic acids, **5b–d**, were reacted under conditions for esters, carbonate **1A** and acetate **2A** afforded diarylmethanes **6Ab–Ad** while halides **3A** and **4A** did not afford **6** (Tables 4 and S4 in ESI[†]). The coupling reactions were not influenced by the electronic properties of the substituents on the boronic acids **5**. On the other hand, **1A** and **2A** were

Table 3 Chemoselective coupling reactions using benzyl carbonates **1** and benzyl chlorides **4**^a



Reactions of esters **1**^b

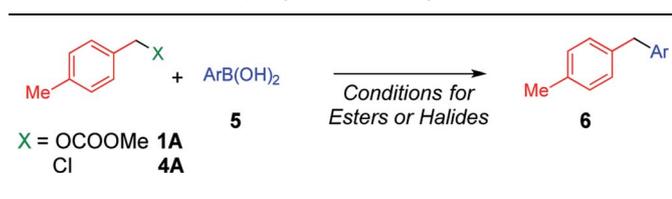
Entry	Benzyl carbonate		Conversion of 1 /%	Product	
	Ar				Yield/%
1	4-	1B	100	6Ba ^{4c}	92
2	MeOC ₆ H ₄	1C	70	6Ca ⁴ⁱ	58
3	4-CF ₃ C ₆ H ₄	1D	49	6Da ^{4f}	41
4	NO ₂ C ₆ H ₄				
5	2-MeC ₆ H ₄	1E	40	6Ea ⁴ⁱ	34
6	2-Pyridyl	1F	81	6Fa ⁸	60
7	2-Furyl	1G	68	6Ga ^{4c}	51
	2-Thienyl	1H	77	6Ha ^{4c}	64

Reactions of halides **4**^c

Entry	Benzyl chloride		Conversion of 4 /%	Product	
	Ar				Yield/%
8	4-	4B	90	6Ba	87
9	MeOC ₆ H ₄			6Ca	70
10	4-CF ₃ C ₆ H ₄	4C	74	6Da	54
11	4-	4D	62		
12	NO ₂ C ₆ H ₄				
13	2-MeC ₆ H ₄	4E	48	6Ea	45
14	2-Pyridyl	4F	73	6Fa	67
	2-Furyl	4G	64	6Ga	52
	2-Thienyl	4H	69	6Ha	64

^a Each reaction was conducted using boronic acid (1.25 equiv.), PdCl₂ (5 mol%). ^b Conditions for esters: DPEPhos (5.5 mol%), NaHCO₃ (2.5 equiv.) in ethanol, at 80 °C for 1 d. ^c Conditions for halides: Ph₃P (11 mol%), Na₂CO₃ (2.5 equiv.) in THF/H₂O (v/v = 1/1), at 40 °C for 1 d.



Table 4 Switchable coupling reaction using other boronic acid^aReactions of ester **1A**^b

Entry	Boronic acid		Conversion of 1 /%	Product	
	Ar				Yield/%
1	4-	5b	87	6Ab ^{6d}	79
2		MeOC ₆ H ₄			
3	4-	5c	86	6Ac ⁹	75
		4-CF ₃ C ₆ H ₄			
	2-	5d	85	6Ad ¹⁰	70
		2-MeC ₆ H ₄			

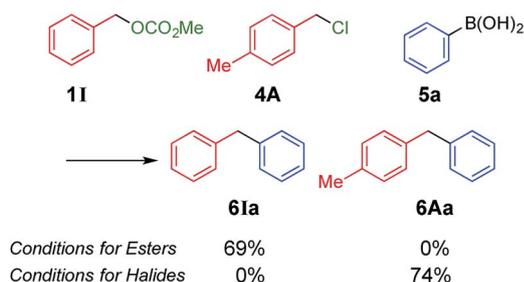
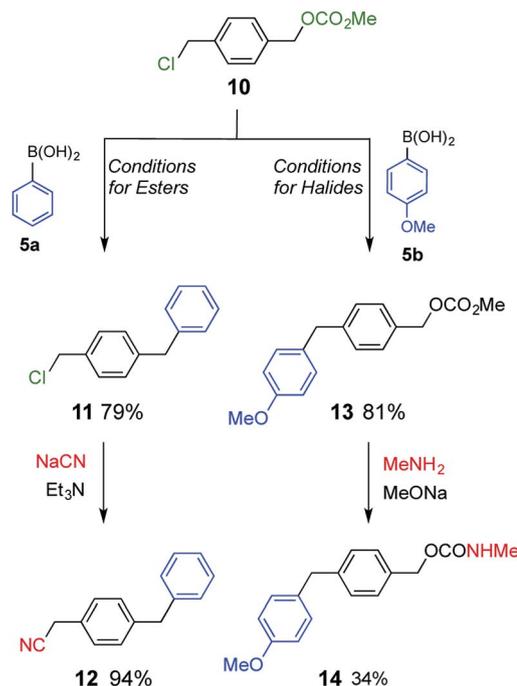
Reactions of halide **4A**^c

Entry	Boronic acid		Conversion of 4 /%	Product	
	Ar				Yield/%
4	4-	5b	70	6Ab	62
		MeOC ₆ H ₄			
5	4-	5c	67	6Ac	60
		4-CF ₃ C ₆ H ₄			
6	2-	5d	66	6Ad	52
		2-MeC ₆ H ₄			

^a Each reaction was conducted using boronic acid (1.25 equiv.), PdCl₂ (5 mol%). ^b Conditions for esters: DPEPhos (5.5 mol%), NaHCO₃ (2.5 equiv.) in ethanol, at 80 °C for 1 d. ^c Conditions for halides: Ph₃P (11 mol%), Na₂CO₃ (2.5 equiv.) in THF/H₂O (v/v = 1/1), at 40 °C for 1 d.

unreactive under conditions for halides. Instead, bromide **3A** and chloride **4A** furnished **6Ab–Ad** in higher yields (Tables 4 and S5 in ESI†). The substrates (benzyl esters or benzyl halides) were successfully switched by changing reaction conditions. Furthermore, the switching mode was not influenced by substituents on the benzene ring of either coupling partner.

Next, we conducted directly competitive reactions of the two substrates (Scheme 3). A mixture of equimolar of benzyl carbonate **1I** and benzyl chloride **4A** was reacted with phenylboronic acid **5a**. When the reaction was conducted under conditions for esters, only carbonate **1I** was consumed to form **6Ia**⁹; **4A** remained unreacted. To the contrary, only chloride **4A** was consumed under conditions for halides. Hence, this switching system was useful even when the reaction mixture contains both benzyl esters and halides.

Scheme 3 Competitive reactions using **1I** and **4A**.Scheme 4 Intramolecular chemoselective coupling reactions of differently substituted compound **10**.

Compound **10**, which possesses both a benzyl ester and benzyl halide moiety was subjected to each of the two reaction conditions (Scheme 4). Compound **11**¹¹ was selectively obtained under conditions for esters. On the other hand, compound **13** was the product when the reaction was carried out under conditions for halides. Product **11** was further converted to benzyl cyanide **12**¹² upon treatment with sodium cyanide, and product **13** was transformed to benzyl carbamate **14** by nucleophilic substitution with methylamine.¹³ As a result, two different classes of compound were synthesized from common starting material **10**.

Conclusions

A chemoselective Suzuki–Miyaura coupling reaction was achieved by switching reaction conditions. Benzyl carbonates **1** and benzyl acetates **2** underwent the coupling reaction with arylboronic acids **5** to afford the corresponding diarylmethanes **6** using a Pd catalyst derived from PdCl₂ and DPEPhos in ethanol in the presence of NaHCO₃ (conditions for esters). Benzyl halides **3** and **4** did not react under the same conditions. On the other hand, when benzyl halides **3** and **4** were reacted using a Pd catalyst derived from PdCl₂ and Ph₃P in THF/water in the presence of Na₂CO₃ (conditions for halides), the coupling reaction efficiently proceeded to afford diarylmethanes **6** while benzyl esters **1** and **2** did not react. This substrate selectivity depends on the different mode of the oxidative addition, and water displaces one of the phosphine ligands. These switchable conditions facilitated the chemoselectivity even when benzyl esters and benzyl halides coexist in a reaction mixture or molecule. The present system will be a useful tool in elaborate syntheses.



Experimental

General

All the reagents and solvents were commercially available and used as received. The ^1H NMR spectra were measured on a JEOL 400 spectrometer at 400 MHz with TMS as an internal standard. The ^{13}C NMR spectra were measured on a JEOL 400 spectrometer at 100 MHz. The IR spectra were recorded on a JASCO FT/IR-4100 spectrometer. The melting points were determined on an As-one melting-points apparatus ATM-02, and were uncorrected. High-resolution mass spectra were obtained on an AB SCEIX Triplet TOF 4600 mass spectrometer. Gas chromatography (GC) was performed with Shimadzu GC 8A. Flash column chromatography was performed with Wako-gel C-200 (100–200 mesh, Wako).

Theoretical calculations for the complexes were carried out with 16W software.¹⁴ Optimizations of the ground-state geometries of the complexes were performed by using the this pro density functional theory (DFT).¹⁵ The LanL2DZ¹⁶ and 6-31G(d,p)¹⁷ basis sets were used to treat the palladium and all other atoms, respectively. Optimized geometries of the complexes were plotted using GaussView 6.0.¹⁸

All diarylmethanes **6**, **11** and **12** are commercially available. Hence, the structures of these products were confirmed by comparison of spectral data with those of authentic samples.

General procedure of the Suzuki–Miyaura coupling reaction under conditions for esters

To a solution of PdCl_2 (1.8 mg, 10 μmol), DPEPhos (5.9 mg, 11 μmol), NaHCO_3 (42.0 mg, 0.5 mmol), and phenylboronic acid **5a** (30.5 mg, 0.25 mmol) in EtOH (1.0 mL), 4-methylbenzyl carbonate **1A** (36.0 mg, 0.2 mmol) was added, and the resultant mixture was heated in a screw-capped sealed tube at 80 °C for 1 d. After treatment with flash column chromatography using hexane to afford **6Aa** (26.6 mg, 0.146 mmol, yield 73%), which is confirmed to be not so different from the yield (76%) determined by ^1H NMR. When other conditions and substrates were employed, the experiments were conducted in a similar way.

General procedure of the Suzuki–Miyaura coupling reaction under conditions for halides

To a solution of PdCl_2 (1.8 mg, 10 μmol), PPh_3 (5.8 mg, 22 μmol), Na_2CO_3 (53.0 mg, 0.5 mmol), and phenylboronic acid **5a** (30.5 mg, 0.25 mmol) in THF and water ($v/v = 1/1$) (1.0 mL), 4-methylbenzyl chloride **4A** (28.1 mg, 0.2 mmol) was added, and the resultant mixture was heated in a screw-capped sealed tube at 40 °C for 1 d. After treatment with flash column chromatography using hexane to afford **6Aa** (28.8 mg, 0.158 mmol, yield 79%), which is confirmed to be not so different from the yield (81%) determined by ^1H NMR. When other conditions and substrates were employed, the experiments were conducted in a similar way.

Intermolecular competitive reaction

Under conditions for esters. To a solution of PdCl_2 (1.8 mg, 10 μmol), DPEPhos (5.9 mg, 11 μmol), NaHCO_3 (42.0 mg, 0.5

mmol), and phenylboronic acid **5a** (30.5 mg, 0.25 mmol) in EtOH (0.5 mL), a solution of benzyl carbonate **1I** (30.0 mg, 0.2 mmol) and 4-methylbenzyl chloride **4A** (28.1 mg, 0.2 mmol) in EtOH (0.5 mL) was added, and the resultant mixture was heated in a screw-capped sealed tube at 80 °C for 1 d. After treatment with flash column chromatography using hexane to afford **6Ia** (23.2 mg, 0.138 mmol, yield 69%) without any detectable **6Aa**.

Under conditions for halides. To a solution of PdCl_2 (1.8 mg, 10 μmol), PPh_3 (5.8 mg, 22 μmol), Na_2CO_3 (53.0 mg, 0.5 mmol), and phenylboronic acid **5a** (30.5 mg, 0.25 mmol) in THF and water ($v/v = 1/1$) (0.5 mL), a solution of benzyl carbonate **1I** (30.0 mg, 0.2 mmol) and 4-methylbenzyl chloride **4A** (28.1 mg, 0.2 mmol) in THF and water ($v/v = 1/1$) (0.5 mL) was added, and the resultant mixture was heated in a screw-capped sealed tube at 40 °C for 1 d. After treatment with flash column chromatography using hexane to afford **6Aa** (26.9 mg, 0.148 mmol, yield 74%) without any detectable **6Ia**.

Chemical conversion of diphenylmethanes

4-[(4-Methoxyphenyl)methyl]phenylmethyl methyl carbonate (13). White solid; mp 176–177 °C. ^1H NMR (CDCl_3 , 400 MHz) δ 7.31 (d, $J = 8.4$ Hz, 2H), 7.23 (d, $J = 8.4$ Hz, 2H), 7.15 (d, $J = 8.4$ Hz, 2H), 6.88 (d, $J = 8.8$ Hz, 2H), 5.08 (s, 2H), 4.21 (s, 2H), 3.79 (s, 3H), 3.76 (s, 3H); ^{13}C NMR (CDCl_3 , 100 MHz) δ 159.9, 156.0, 137.2, 130.4, 129.2, 127.5, 127.2, 114.0, 113.7, 69.6, 55.3, 54.9, 40.6; IR (neat) 3473, 2958, 1747, 1613, 1515, 1442, 1377, 1247 cm^{-1} ; HRMS (ESI-TOF) m/z [$\text{M} + \text{Na}$]⁺ calcd for $\text{C}_{17}\text{H}_{18}\text{O}_4\text{Na}$ 309.1097; found 309.1099.

Cyanation of benzyl chloride 11. To a solution of benzyl chloride **11** (216 mg, 1.0 mmol) in DMSO (2 mL), were added sodium cyanide (147 mg, 3.0 mmol) and triethylamine (304 mg, 3.0 mmol), and the resultant mixture was heated at 80 °C for 1 d. After filtration using a Celite pad, the filtrate was extracted with ethyl acetate (10 mL \times 3). The combined organic layer was washed with brine (10 mL \times 1), dried over MgSO_4 , and concentrated under reduced pressure. The residue was treated with flash column chromatography (EtOAc/hexane = 20/80) to afford benzyl cyanide **12** (194 mg, 0.94 mmol, yield 94%).

4-[(4-Methoxyphenyl)methyl]phenylmethyl methyl carbamate (14). To a solution of carbonate **13** (286 mg, 1.0 mmol) in toluene (2 mL), were added methylamine (31.1 mg, 1.0 mmol) and sodium methoxide (54 mg, 1.0 mmol), and the resultant mixture was heated at 80 °C for 1 d. After filtration using a Celite pad, the filtrate was extracted with ethyl acetate (10 mL \times 3). The combined organic layer was washed with brine (10 mL \times 1), dried over MgSO_4 , and concentrated under reduced pressure. The residue was treated with flash column chromatography (EtOAc/hexane = 50/50) to afford carbamate **14** (96 mg, 0.34 mmol, yield 34%). White solid; mp 94–95 °C. ^1H NMR (CDCl_3 , 400 MHz) δ 7.28 (d, $J = 8.8$ Hz, 2H), 7.20 (d, $J = 8.4$ Hz, 2H), 7.11 (d, $J = 8.0$ Hz, 2H), 6.85 (d, $J = 8.8$ Hz, 2H), 6.1–6.3 (br, 1H), 5.04 (s, 2H), 4.19 (s, 2H), 3.72 (s, 3H), 2.69 (s, 3H); ^{13}C NMR (CDCl_3 , 100 MHz) δ 159.9, 155.9, 137.1, 130.4, 129.2, 127.5, 127.2, 114.3, 113.7, 68.4, 54.9, 40.8, 21.2; IR (neat) 3319, 2957, 1747, 1657, 1515, 1443, 1273 cm^{-1} ; HRMS (ESI-TOF) m/z [$\text{M} + \text{Na}$]⁺ calcd for $\text{C}_{17}\text{H}_{19}\text{NO}_3\text{Na}$ 308.1257, found 308.1258.



Conflicts of interest

There are no conflicts to declare.

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