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Palladium-Catalyzed Benzylation of Arylboronic Acids with *N,N*-Ditosylbenzylamines

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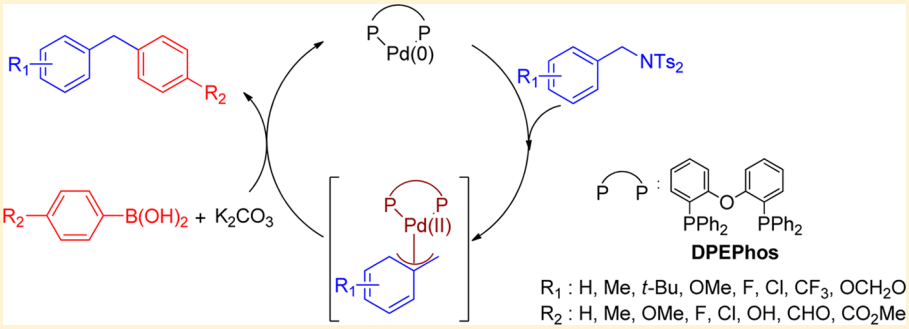
Supporting Information



ABSTRACT: The palladium-catalyzed coupling of *N,N*-ditosylbenzylamines with arylboronic acids has been investigated, and the resulting diarylmethanes were obtained in high yields. Conversion of the amine to a *N,N*-ditosylimide group provided an efficient leaving group for the Pd-catalyzed benzylation of arylboronic acids.

A variety of Pd-catalyzed reactions have been developed over the past several decades. Pd-catalyzed cross-coupling reactions provide efficient methods to construct new C−C bonds or to introduce functional groups into organic molecules.[1] Recently, Pd-catalyzed benzylations that combine benzylic halides,[2] carbonates,[3] or phosphates[4] with an aryl counterpart have been reported,[5] and the resulting diarylmethane products are found as substructures in molecules with pharmaceutical activity[6] and supramolecules.[7]

In general, the amino group is known to be a poor leaving group in metal-catalyzed coupling reactions, as it is difficult to cleave the C−N bond in the reaction process. Until now, only two groups have reported metal-catalyzed coupling reactions of benzylic amines with aryl compounds by C−N bond activation. One group demonstrated a nickel-catalyzed cross-coupling of benzylic ammonium triflates with aryl boronic acids.[8] Another group investigated a copper(I)-catalyzed coupling of Grignard reagents with benzylic sulfonylimides.[9] Previously, our group reported the Pd(0)-catalyzed coupling reaction of *N,N*-ditosylallylamine with nucleophiles (Figure 1, eq 1).[10] The allylic *N,N*-ditosylimide group has been utilized in the synthesis of carbocyclic nucleosides via the formation of π-allylpalladium complexes.[11]

Building on previous research results of the Tsuji−Trost reaction with *N,N*-ditosylallylamine, herein, we wish to disclose the first Pd-catalyzed coupling of *N,N*-ditosylbenzylamines **1** with arylboronic acids (eq 2).

In order to generalize the Pd-catalyzed coupling reaction, a variety of *N,N*-ditosylbenzylamines **1** were prepared from the corresponding benzylamine as shown in Scheme 1.[12] Conditions for the coupling reaction were then optimized using *N,N*-ditosylbenzylamine **1a** and phenylboronic acid **2a** (Table 1).

First, the cross-coupling reaction was attempted with an *in situ* generated Pd(0)-catalyst, which we had used in previous work;[10,11a,c] however, the reaction did not proceed in this case (entry 1). Next, various phosphine ligands were screened with the $[Pd(allyl)Cl]_2$ catalyst and K_2CO_3 at 60 °C in DMF (entries 2−10). It was found that DPEPhos was a suitable phosphine ligand, affording the coupled product **3a** in 93% yield (entry 10). Coupling reactions were carried out with different bases (entries 10−13), and subsequently, several Pd catalysts were screened (entries 10, 14−19) to optimize the reaction. With the $Pd(CH_3CN)_4(BF_4)_2$ catalyst, DPEPhos ligand, and K_2CO_3 base, the reaction generated the coupled product **3a** in the highest yield in addition to requiring a shorter reaction time (entry 19).

Using the optimized conditions (Table 1, entry 19), the Pd-catalyzed benzylation was applied to a broad group of both *N,N*-ditosylbenzylamine **1** and arylboronic acid **2** substrates (Table 2). Most of the reactions afforded diarylmethanes **3** in good to excellent yields. With the 4-chloro- and 4-bromo-substituted *N,N*-ditosylbenzyl amines (**1e**, **1f**), the Suzuki−Miyaura coupling product 4-benzylbiphenyl **4** was obtained as a side product (entries 5, 6). While *N,N*-ditosyl-4-chlorobenzylamine **1e** afforded the desired coupling product **3e** as the major

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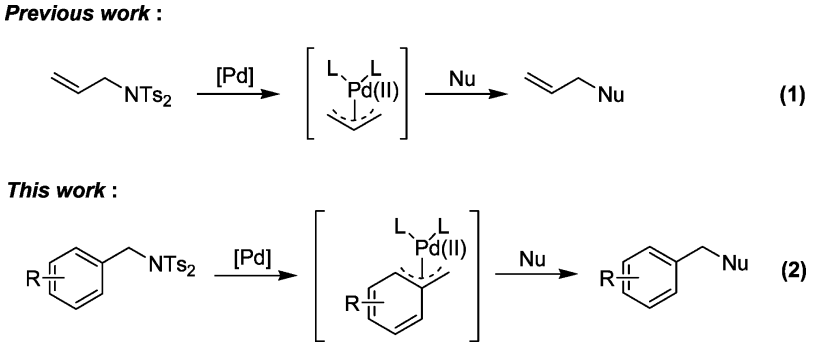
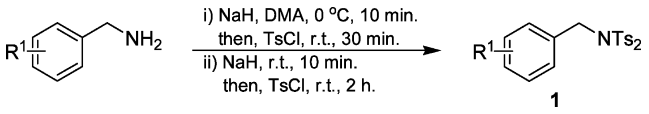


Figure 1. Palladium-catalyzed coupling of *N,N*-ditosylallylamine and *N,N*-ditosylbenzylamines.

Scheme 1. Preparation of *N,N*-Ditosylbenzylamines



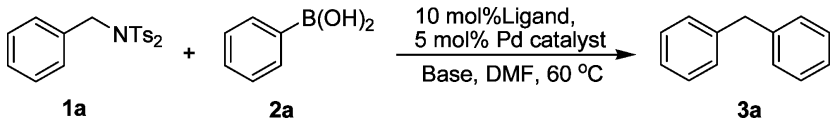
product (entry 5), only a trace amount of the desired product **3f** was obtained in the reaction with *N,N*-ditosyl-4-bromobenzylamine **1f** (entry 6). This result suggests that bromide at aryl C−Br is a better leaving group than either chloride at aryl C−Cl or *N,N*-ditosylimide at benzylic C-NTs_2. With the exception of entry 6, both electron-donating (entries 1−4, 9) and electron-withdrawing groups (entries 5, 7, 8) were tolerated in the reaction.

From various arylboronic acids **2**, diarylmethanes **3** were obtained in high yields without contamination of the 4-benzylbiphenyl byproduct (entries 10−16). From the above results, these reaction conditions tolerated a variety of functional groups, including alkyl, ether, chloride, fluoride, trifluoromethyl, acetal, hydroxy, aldehyde, and ester groups.

Based on our previous work and others,[2h,10,13] we assume that the Pd-catalyzed benzylation of arylboronic acids **2** with *N,N*-ditosylbenzylamines **1** follows the Tsuji−Trost type mechanism (Scheme 2). An *in situ* generated Pd(0)-catalyst coordinates to the benzylic compound **1**, followed by oxidative addition to afford (η^3-benzyl)palladium(II) **I**. This reaction pathway is similar to the formation of the π-allylpalladium complex from *N,N*-ditosylallylamine. Following transmetalation with arylboronic acid and subsequent reductive elimination, diarylmethane **3** is formed.

In summary, we have developed a new Pd-catalyzed benzylation reaction that utilizes *N,N*-ditosylimide as a leaving group. In this coupling reaction, diarylmethanes **3** were obtained in high yields. The reaction results indicate that our new catalytic system provides an efficient method for the cross-coupling of *N,N*-ditosylbenzylamines with arylboronic acids.

Table 1. Optimization of Reaction Conditions[a]



entry	ligand	Pd catalyst	base	time, h	yield, %
1	$(i\text{-PrO})_3P$	Pd(0)[b]	–	5	–
2	PCy_3	$[Pd(allyl)Cl]_2$	K_2CO_3	6	–
3	PPh_3	$[Pd(allyl)Cl]_2$	K_2CO_3	6	14
4	JohnPhos	$[Pd(allyl)Cl]_2$	K_2CO_3	6	87
5	*t*-Bu XPhos	$[Pd(allyl)Cl]_2$	K_2CO_3	6	76
6	SPhos	$[Pd(allyl)Cl]_2$	K_2CO_3	6	47
7	RuPhos	$[Pd(allyl)Cl]_2$	K_2CO_3	6	47
8	DPPE	$[Pd(allyl)Cl]_2$	K_2CO_3	6	81
9	XantPhos	$[Pd(allyl)Cl]_2$	K_2CO_3	6	79
10	DPEPhos	$[Pd(allyl)Cl]_2$	K_2CO_3	6	93
11	DPEPhos	$[Pd(allyl)Cl]_2$	Cs_2CO_3	6	46
12	DPEPhos	$[Pd(allyl)Cl]_2$	K_3PO_4	6	54
13	DPEPhos	$[Pd(allyl)Cl]_2$	TEA	6	–
14	DPEPhos	$Pd_2(dba)_3$	K_2CO_3	6	1
15	DPEPhos	$Pd(OAc)_2$	K_2CO_3	6	82
16	DPEPhos	$PdCl_2$	K_2CO_3	6	73
17	DPEPhos	K_2PdCl_4	K_2CO_3	6	6
18	DPEPhos	$Pd(CH_3CN)_2Cl_2$	K_2CO_3	6	77
19	DPEPhos	$Pd(CH_3CN)_4(BF_4)_2$	K_2CO_3	3	96

[a]Conditions: *N,N*-ditosylbenzylamine **1a** (1.0 equiv), phenylboronic acid **2a** (1.5 equiv), ligand (10 mol %), Pd catalyst (5 mol %), base (3.0 equiv), DMF (0.3 M) at 60 °C. [b]Pd(0) catalyst was prepared *in situ* from $Pd(OAc)_2$, $(i\text{-PrO})_3P$, and *n*-BuLi in THF.

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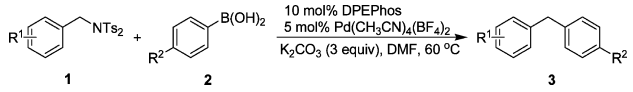
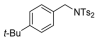
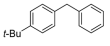
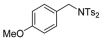
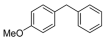
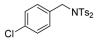
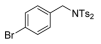
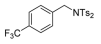
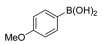
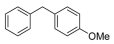
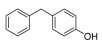
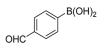
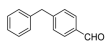
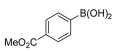
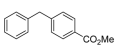
Table 2. Cross-coupling of *N,N*-Ditosylbenzylamines (1) with Arylboronic Acids (2)[a]



1 2 3

entry	1	2	time, h	Product 3	yield, %
1	 **1a**	 **2a**	3	 **3a**	96
2	 **1b**	**2a**	3	 **3b**	99
3	 **1c**	**2a**	3	 **3c**	99
4	 **1d**	**2a**	4	 **3d**	87
5	 **1e**	**2a**	3	 **3e**	79(9)[b]
6	 **1f**	**2a**	8	 **3f**	trace(21)[b]
7	 **1g**	**2a**	3	 **3g**	80
8	 **1h**	**2a**	1	 **3h**	71
9	 **1i**	**2a**	6	 **3i**	85
10	**1a**	 **2b**	3	 **3b**	99
11	**1a**	 **2d**	3	 **3d**	98
12	**1a**	 **2e**	9	 **3e**	82
13	**1a**	 **2g**	5	 **3g**	89
14	**1a**	 **2j**	5	 **3j**	90
15	**1a**	 **2k**	1.5	 **3k**	99
16	**1a**	 **2l**	2	 **3l**	98

[a]Conditions: *N,N*-ditosylbenzylamine **1** (1.0 equiv), arylboronic acid **2** (1.5 equiv), DPEPhos (10 mol %), $Pd(CH_3CN)_4(BF_4)_2$ (5 mol %), K_2CO_3 (3.0 equiv), DMF (0.3 M) at 60 °C. [b]4-Benzylbiphenyl **4** was also obtained.

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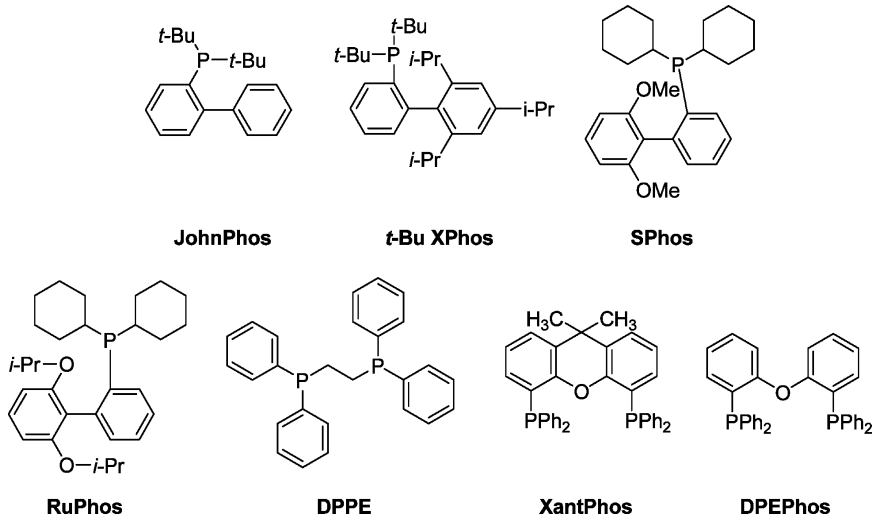
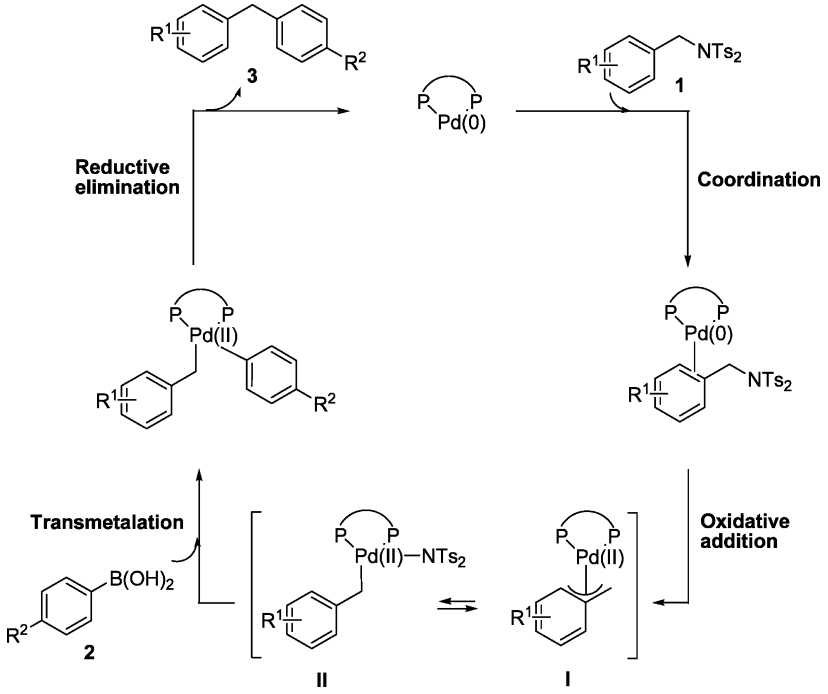


Figure 2. Various phosphine ligands used in coupling reactions.

Scheme 2. Presumed Mechanism



EXPERIMENTAL SECTION

General Information. ^{1}H and ^{13}C NMR spectra were obtained in $CDCl_3$ with a spectrometer operating at 400 MHz for ^{1}H and 100 MHz for ^{13}C with TMS as an internal standard. Chemical shifts (δ) and coupling constants (J) are expressed in ppm and Hz, respectively. Infrared (IR) spectra were recorded on an FT-IR spectrometer. Melting points were determined with a melting point apparatus. High resolution mass spectra (HRMS) were obtained on a mass spectrometer with double-focusing mass analyzers. Analytical thin layer chromatography (TLC) was conducted on aluminum-backed silica gel plates with compounds observed by UV lamp illumination or by staining with ninhydrin, phosphomolybdic acid (PMA), or $KMnO_4$. Flash column chromatography was performed using silica gel (230–400 mesh) under positive pressure. Commercially obtained reagents were used without further purification. All coupling reactions were carried out in flame-dried flasks under an argon atmosphere.

General Procedure for the Preparation of Starting Materials. The benzylamine (3.0 mmol) and sodium hydride (60% dispersion in mineral oil, 0.150 g, 3.75 mmol) were added to *N,N*-dimethylacetamide (12 mL) under an argon atmosphere in a two-necked flask at 0 °C, and the solution was stirred for 10 min. *p*-Toluenesulfonyl chloride (0.715 g, 3.75 mmol) was added to the reaction, and the mixture was stirred for 30 min at ambient temperature. Sodium hydride (60% dispersion in mineral oil, 0.150 g, 3.75 mmol) was added to the solution at ambient temperature, and after the mixture was stirred for 10 min, *p*-toluenesulfonyl chloride (0.715 g, 3.75 mmol) was added. After stirring for 2 h, the reaction was quenched with ice water (30 mL), and the resulting solid material was collected by vacuum filtration and dried in a vacuum drying oven to afford *N,N*-ditosylbenzylamines.

***N,N*-Ditosylbenzylamine (1a).**[9] Compound **1a** (1.2015 g, 96%) was obtained as a white solid. ^{1}H NMR (400 MHz, $CDCl_3$, ppm): δ 7.66–7.63 (m, 4H), 7.40–7.37 (m, 2H), 7.30–7.23 (m, 3H), 7.22–7.19 (m, 4H), 4.89 (s, 2H), 2.40 (s, 6H).

***N,N*-Ditosyl-4-methylbenzylamine (1b).**[14] Compound **1b** (1.2886 g, 99%) was obtained as a white solid. ^{1}H NMR (400 MHz, $CDCl_3$, ppm): δ 7.67–7.64 (m, 4H), 7.27 (d, J = 7.6 Hz, 2H), 7.22–

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7.20 (m, 4H), 7.05 (d, J = 7.6 Hz, 4H), 4.85 (s, 2H), 2.41 (s, 6H), 2.34 (s, 3H).

***N,N*-Ditosyl-4-*tert*-butylbenzylamine (1c).** Compound **1c** (1.4008 g, 99%) was obtained as a white solid. Mp 143−145 °C; ^{1}H NMR (400 MHz, $CDCl_3$, ppm): δ 7.63 (d, J = 8.4 Hz, 4H), 7.30 (d, J = 8.4 Hz, 2H), 7.26−7.23 (m, 2H), 7.18 (d, J = 8.0 Hz, 4H), 4.89 (s, 2H), 2.40 (s, 6H), 1.32 (s, 9H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$, ppm): δ 151.2, 144.6, 137.4, 131.7, 129.4, 129.1, 128.2, 125.3, 52.3, 34.7, 31.5, 21.8; IR (ν_{max}/cm^{-1}): 3032, 2959, 2923, 2854, 1597, 1464, 1367, 1352, 1163, 1083, 1040, 1017, 994, 811, 788, 658, 594, 544; HRMS (EI): m/z (M$^+$) Calcd for $C_{25}H_{29}NO_4S_2$, 471.1538. Found 471.1541.

***N,N*-Ditosyl-4-methoxybenzylamine (1d).[9]** Compound **1d** (1.3092 g, 98%) was obtained as a white solid. ^{1}H NMR (400 MHz, $CDCl_3$, ppm): δ 7.66−7.64 (m, 4H), 7.35−7.32 (m, 2H), 7.22 (d, J = 8.0 Hz, 4H), 6.80−6.77 (m, 2H), 4.83 (s, 2H), 3.81 (s, 3H), 2.41 (s, 6H).

***N,N*-Ditosyl-4-chlorobenzylamine (1e).[9]** Compound **1e** (1.2496 g, 93%) was obtained as a white solid. ^{1}H NMR (400 MHz, $CDCl_3$, ppm): δ 7.67−7.65 (m, 4H), 7.32−7.29 (m, 2H), 7.25−7.19 (m, 6H), 4.85 (s, 2H), 2.42 (s, 6H).

***N,N*-Ditosyl-4-bromobenzylamine (1f).[9]** 4-Bromobenzyl amine HCl (0.668 g, 3.0 mmol) was dissolved in H_2O and treated with Na_2CO_3. The reaction solution was extracted with CH_2Cl_2, dried over anhydrous $MgSO_4$, filtered, and evaporated to obtain free 4-bromobenzylamine. The general procedure was conducted with 4-bromobenzylamine, and **1f** (1.2444 g, 83%) was obtained as a white solid. ^{1}H NMR (400 MHz, $CDCl_3$, ppm): δ 7.68−7.65 (m, 4H), 7.37−7.34 (m, 2H), 7.25−7.23 (m, 6H), 4.83 (s, 2H), 2.43 (s, 6H).

***N,N*-Ditosyl-4-fluorobenzylamine (1g).[9]** Compound **1g** (1.2819 g, 98%) was obtained as a white solid. ^{1}H NMR (400 MHz, $CDCl_3$, ppm): δ 7.67−7.64 (m, 4H), 7.40−7.35 (m, 2H), 7.23 (d, J = 8.4 Hz, 4H), 6.97−6.91 (m, 2H), 4.85 (s, 2H), 2.42 (s, 6H).

***N,N*-Ditosyl-4-trifluoromethylbenzylamine (1h).** Compound **1h** (1.3029 g, 89%) was obtained as a white solid. Mp 136−137 °C; ^{1}H NMR (400 MHz, $CDCl_3$, ppm): δ 7.66 (d, J = 8.4 Hz, 4H), 7.47−7.43 (m, 4H), 7.21 (d, J = 8.0 Hz, 4H), 4.95 (s, 2H), 2.41 (s, 6H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$, ppm): δ 145.0, 138.8, 136.9, 130.2 (q, J = 32 Hz), 129.5, 129.3, 128.1, 125.2 (q, J = 3.7 Hz), 124.0 (q, J = 271 Hz), 51.7, 21.6; IR (ν_{max}/cm^{-1}): 3065, 2923, 2853, 1619, 1595, 1492, 1445, 1350, 1324, 1161, 1112, 1068, 1048, 1004, 829, 814, 661, 546; HRMS (EI): m/z (M$^+$) Calcd for $C_{22}H_{20}F_3NO_4S_2$, 483.0786. Found 483.0785.

5-*N,N*-Ditosylaminomethyl-1,3-benzodioxole (1i). Compound **1i** (1.2852 g, 93%) was obtained as a pale yellow solid. Mp 149−150 °C (dec.); ^{1}H NMR (400 MHz, $CDCl_3$, ppm): δ 7.7 (d, J = 8.4 Hz, 4H), 7.24 (d, J = 8.0 Hz, 4H), 6.89−6.87 (m, 2H), 6.71−6.69 (m, 1H), 5.93 (s, 2H), 4.80 (s, 2H), 2.42 (s, 6H); ^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$, ppm): δ 147.8, 147.5, 144.8, 137.3, 129.5, 128.7, 128.2, 123.3, 109.8, 108.0, 101.2, 52.3, 21.8; IR (ν_{max}/cm^{-1}): 3071, 2922, 2853, 1596, 1488, 1447, 1367, 1346, 1291, 1242, 1164, 1084, 1021, 996, 925, 828, 807, 761, 657, 538; HRMS (EI): m/z (M$^+$) Calcd for $C_{22}H_{21}NO_6S_2$, 459.0810. Found 459.0812.

General Procedure for the Coupling Reaction of *N,N*-Ditosylbenzylamines 1 with Arylboronic Acids 2. DPEPhos (98%, 0.0539 g, 0.1 mmol) and $Pd(CH_3CN)_4(BF_4)_2$ (0.0222 g, 0.05 mmol) were added to anhydrous DMF (3.0 mL) under an argon atmosphere in a two-necked flask, and the resulting solution was stirred at ambient temperature for 5 min. The *N,N*-ditosylbenzylamine derivative (1.0 mmol), arylboronic acid (1.5 mmol), and K_2CO_3 (0.4146 g, 3.0 mmol) were added, and the mixture was heated at 60 °C. When TLC indicated the absence of the *N,N*-ditosylbenzylamine derivative or the color of the reaction solution turned dark brown, the mixture was cooled to ambient temperature. The solution was extracted with hexane, washed with brine, dried over anhydrous $MgSO_4$, filtered, and evaporated to afford the crude mixture. The crude product mixture was purified by SiO_2 gel flash column chromatography (ethyl acetate/hexane) to yield the diarylmethane.

Diphenylmethane (3a).[8] After purification by SiO_2 gel flash column chromatography with hexane as the eluent, **3a** (0.1615 g, 96%) was obtained as a colorless liquid. ^{1}H NMR (400 MHz, $CDCl_3$, ppm): δ 7.30−7.26 (m, 4H), 7.22−7.17 (m, 6H), 3.98 (s, 2H).

1-Benzyl-4-methylbenzene (3b).[8] After purification of the reaction mixture from *N,N*-ditosyl-4-methyl-benzylamine **1b** (0.4295 g, 1.0 mmol) and phenylboronic acid **2a** (0.1829 g, 1.5 mmol) by SiO_2 gel flash column chromatography with hexane as the eluent, **3b** (0.1804 g, 99%) was obtained as a colorless liquid. The reaction of *N,N*-ditosylbenzylamine **1a** (0.4155 g, 1.0 mmol) with 4-methylphenylboronic acid **2b** (0.2039 g, 1.5 mmol) afforded the same product (0.1803 g, 99%) as a colorless liquid. ^{1}H NMR (400 MHz, $CDCl_3$, ppm): δ 7.31−7.28 (m, 2H), 7.22−7.19 (m, 3H), 7.130−7.08 (m, 4H), 3.96 (s, 2H), 2.33 (s, 3H).

1-Benzyl-4-*tert*-butylbenzene (3c).[2e] After purification by SiO_2 gel flash column chromatography with hexane as the eluent, **3c** (0.2223 g, 99%) was obtained as a yellowish liquid. ^{1}H NMR (400 MHz, $CDCl_3$, ppm): δ 7.34−7.28 (m, 4H), 7.23−7.19 (m, 3H), 7.15−7.12 (m, 2H), 3.97 (s, 2H), 1.31 (s, 9H).

1-Benzyl-4-methoxybenzene (3d).[8] After purification of the reaction mixture from *N,N*-ditosyl-4-methoxy-benzylamine **1d** (0.4556 g, 1.0 mmol) and phenylboronic acid **2a** (0.1829 g, 1.5 mmol) by SiO_2 gel flash column chromatography with hexane as the eluent, **3d** (0.1729 g, 87%) was obtained as a colorless liquid. The reaction of *N,N*-ditosylbenzylamine **1a** (0.4155 g, 1.0 mmol) with 4-methoxyphenylboronic acid **2d** (0.2279 g, 1.5 mmol) afforded the same product (0.1958 g, 98%) as a colorless liquid. ^{1}H NMR (400 MHz, $CDCl_3$, ppm): δ 7.43−7.39 (m, 2H), 7.33−7.30 (m, 3H), 7.25−7.22 (m, 2H), 6.98−6.95 (m, 2H), 4.05 (s, 2H), 3.88 (s, 3H).

1-Benzyl-4-chlorobenzene (3e).[4a] After purification of the reaction mixture from *N,N*-ditosyl-4-chloro-benzylamine **1e** (0.4500 g, 1.0 mmol) and phenylboronic acid **2a** (0.1829 g, 1.5 mmol) by SiO_2 gel flash column chromatography with hexane as the eluent, **3e** (0.1610 g, 79%) was obtained as a colorless liquid. The reaction of *N,N*-ditosylbenzylamine **1a** (0.4155 g, 1.0 mmol) with 4-chlorophenylboronic acid **2e** (0.2346 g, 1.5 mmol) afforded the same product (0.1662 g, 82%) as a colorless liquid. ^{1}H NMR (400 MHz, $CDCl_3$, ppm): δ 7.45−7.33 (m, 5H), 7.31−7.29 (m, 2H), 7.25−7.22 (m, 2H), 4.07 (s, 2H).

1-Benzyl-4-fluorobenzene (3g).[8] After purification of the reaction mixture from *N,N*-ditosyl-4-fluorobenzylamine **1g** (0.4335 g, 1.0 mmol) and phenylboronic acid **2a** (0.1829 g, 1.5 mmol) by SiO_2 gel flash column chromatography with hexane as the eluent, **3g** (0.1491 g, 80%) was obtained as a yellow liquid. The reaction of *N,N*-ditosylbenzylamine **1a** (0.4155 g, 1.0 mmol) with 4-fluorophenylboronic acid **2g** (0.2100 g, 1.5 mmol) afforded the same product (0.1660 g, 89%) as a yellow liquid. ^{1}H NMR (400 MHz, $CDCl_3$, ppm): δ 7.31−7.27 (m, 2H), 7.22−7.16 (m, 5H), 6.98−6.94 (m, 2H), 3.95 (s, 2H).

1-Benzyl-4-trifluoromethylbenzene (3h).[8] After purification by SiO_2 gel flash column chromatography with hexane as the eluent, **3h** (0.1668 g, 71%) was obtained as a colorless liquid. ^{1}H NMR (400 MHz, $CDCl_3$, ppm): δ 7.54 (d, J = 8.0 Hz, 2H), 7.33−7.29 (m, 4H), 7.25−7.21 (m, 1H), 7.19−7.17 (m, 2H), 4.04 (s, 2H).

5-Benzyl-1,3-benzodioxole (3i).[8] After purification by SiO_2 gel flash column chromatography with ethyl acetate/hexane as the eluent (1/99, v/v), **3i** (0.1807 g, 85%) was obtained as a colorless liquid. ^{1}H NMR (400 MHz, $CDCl_3$, ppm): δ 7.28−7.24 (m, 2H), 7.19−7.15 (m, 3H), 6.72−6.70 (m, 1H), 6.64−6.63 (m, 2H), 5.86 (s, 2H), 3.86 (s, 2H).

4-Benzylphenol (3j).[2e] After purification by SiO_2 gel flash column chromatography with ethyl acetate/hexane as the eluent (1/7, v/v), **3j** (0.1660 g, 90%) was obtained as a pale yellow solid. ^{1}H NMR (400 MHz, $CDCl_3$, ppm): δ 7.30−7.23 (m, 2H), 7.18−7.13 (m, 3H), 7.02−7.00 (m, 2H), 6.72−6.70 (m, 2H), 5.44 (br. s, 1H), 3.87 (s, 2H).

4-Benzylbenzaldehyde (3k).[2b] After purification by SiO_2 gel flash column chromatography with ethyl acetate/hexane as the eluent (1/7, v/v), **3k** (0.1943 g, 99%) was obtained as a yellow liquid. ^{1}H NMR (400 MHz, $CDCl_3$, ppm): δ 9.95 (s, 1H), 7.79 (d, J = 8.0 Hz, 2H), 7.34−7.28 (m, 4H), 7.24−7.16 (m, 3H), 4.04 (s, 2H).

Methyl 4-Benzylbenzoate (3l).[8] After purification by SiO_2 gel flash column chromatography with ethyl acetate/hexane as the eluent

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(1/10, v/v), **3l** (0.2207 g, 98%) was obtained as a colorless liquid. ^{1}H NMR (400 MHz, $CDCl_3$, ppm): δ 7.94 (d, J = 8.0 Hz, 2H), 7.28−7.13 (m, 7H), 3.98 (s, 2H), 3.85 (s, 3H).

■ ASSOCIATED CONTENT

Supporting Information

General procedure and spectral data (^{1}H NMR for all compounds and ^{13}C{^{1}H} NMR, IR, HRMS for compounds **1c**, **1h**, and **1i**) are provided in the Supporting Information. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

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