JOC*Note*

Cationic Pd(II)/Bipyridine-Catalyzed Addition of Arylboronic Acids to Arylaldehydes. One-Pot Synthesis of Unsymmetrical Triarylmethanes

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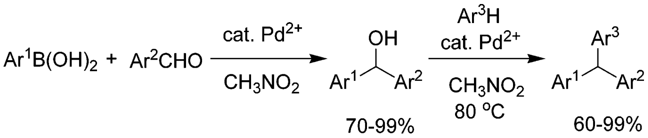
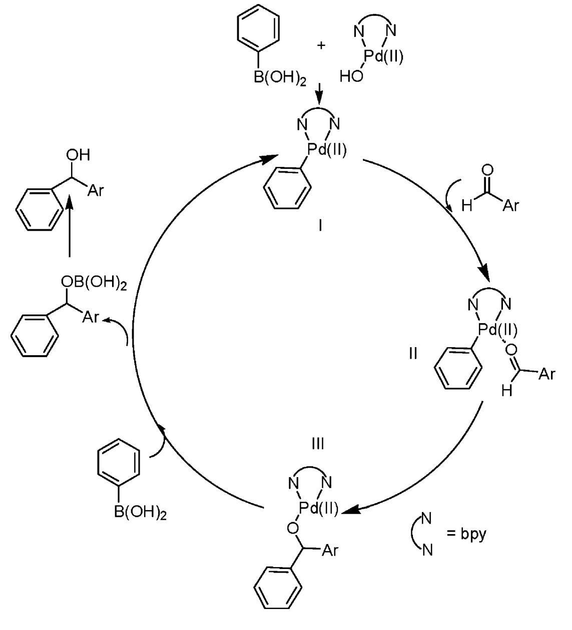


Cationic Pd(II) complex-catalyzed addition of arylboronic acids to aldehydes with low catalyst loading was developed with high yields. One-pot synthesis of unsymmetrical triarylmethanes from arylboronic acids, aryl aldehydes, and electron-rich arenes was achieved in high yields.

Transition metal catalysis provides powerful tools for carbon−carbon bond construction.[1] Recent reports on Rh(I)-catalyzed addition reactions of arylboronic acids to various electrophiles[2] prompted us to examine the Pd(II)-catalyzed nucleophilic addition reactions of arylboronic acids. Compared with numerous reports of Rh(I)-catalyzed addition reactions to aldehydes, ketones, imines, and nitriles, Pd(II)-catalyzed nucleophilic addition reactions of arylboronic acids are relatively rare.[3] While arylrhodium species are more nucleophilic and capable of addition to electrophiles, arylpalladium species are more electrophilic.[4] For the palladium catalysts, it is worth mentioning that Miyaura reported the conjugate addition of arylboronic acids to enones catalyzed by cationic Pd(II) complex with phosphine ligands.[5a,b] In our previous work, we found that bidentate nitrogen ligands such as 2,2′-bipyridine (bpy), phenanthroline, and dioxazolines could stabilize the Pd(II) species.[6] We reported the Pd(II)/bpy-catalyzed addition of alkenylpalladium species, formed by the acetoxypalladation of the alkynes, to α,β-unsaturated carbonyl compounds,[6d,e] ketones,[6f] and nitriles.[6f] It was suggested that the electron-donating property of the ligands would make the organopalladium species more nucleophilic, and would favor the nucleophilic addition.[3,4] On the basis of this suggestion, we successfully developed the Pd(II)/bpy-catalyzed addition of arylboronic acids to α,β-unsaturated carbonyl compounds[7a] and nitriles[7b] with high yields and also the cationic Pd(II)/bpy-catalyzed one-step synthesis of benzofurans from phenoxyacetonitriles.[8a] In all these reactions, bpy was used as the ligand making the nucleophilic addition of arylboronic acids to carbon−heteroatom multiple bonds successful. It was also found that the cationic Pd(II) species with chiral phosphine ligand could catalyze the intramolecular addition of arylboronic acids to ketones with excellent yields and high ee values.[8b] These examples showed that cationic Pd(II) complexes are excellent catalysts for the addition of arylboronic acids to carbon−heteroatom multiple bonds due to their high Lewis acidity and existence of vacant coordination sites.[8]

SCHEME 1. Proposed Mechanism for the Addition of Arylboronic Acids to Arylaldehydes Catalyzed by Catalyst A2



Miyaura reported the first Rh(I)-catalyzed addition of arylboronic acids to aldehydes[9a,b] and the asymmetric version of this reaction with moderate ee values has been reported by some

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(1) (a) de Meijere, A.; Diederich, F. *Metal-Catalyzed Cross-Coupling Reactions*, 2nd ed.; Wiley-VCH: Weinheim, Germany, 2004. (b) Beller, M.; Bolm, C. *Transition Metals for Organic Synthesis*: *Building Blocks and Fine Chemicals*; Wiley-VCH: New York, 1998.

(2) (a) Fagnou, K.; Lautens, M. *Chem. Rev.* **2003**, *103*, 169. (b) Hayashi, T.; Yamasaki, K. *Chem. Rev.* **2003**, *103*, 2829.

(3) Yamamoto, Y.; Nishikata, T.; Miyaura, N. *J. Synth. Org. Chem., Jpn.* **2006**, *64*, 1112.

(4) Ueura, K.; Satoh, T.; Miura, M. *Org. Lett.* **2005**, *7*, 2229.

(5) (a) Nishikata, T.; Yamamoto, Y.; Miyaura, N. *Angew. Chem., Int. Ed.* **2003**, *42*, 2768. (b) Nishikata, T.; Yamamoto, Y.; Miyaura, N. *Organometallics* **2004**, *23*, 4317.

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(7) (a) Lu, X.; Lin, S. *J. Org. Chem.* **2005**, *70*, 9651. (b) Zhao, B.; Lu, X. *Tetrahedron Lett.* **2006**, *47*, 6765.

(8) (a) Zhao, B.; Lu, X. *Org. Lett.* **2006**, *8*, 5987. (b) Liu, G.; Lu, X. *J. Am. Chem. Soc.* **2006**, *128*, 16504.

(9) (a) Sakai, M.; Ueda, M.; Miyaura, N. *Angew. Chem., Int. Ed.* **1998**, *37*, 3279. (b) Ueda, M.; Miyaura, N. *J. Org. Chem.* **2000**, *65*, 4450. (c) Moreau, C.; Hague, C.; Weller, A. S.; Frost, C. G. *Tetrahedron Lett.* **2001**, *42*, 6957. (d) Fuchen, T.; Rudolph, J.; Bolm, C. *Synthesis* **2005**, 429. (e) Duan, H.; Xie, J.; Shi, W.; Zhang, Q.; Zhou, Q. *Org. Lett.* **2006**, *8*, 1479. (f) Jagt, R. B. C.; Toullec, P. Y.; de Vries, J. G.; Feringa, B. L.; Minnaard, A. J. *Org. Biomol. Chem.* **2006**, *4*, 773.

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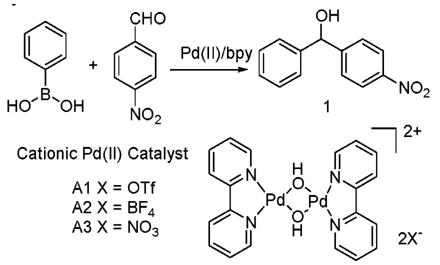
TABLE 1. Cationic Pd(II)-Catalyzed Addition of Phenylboronic Acid to 4-Nitrobenzaldehyde[a]



entry	catalyst	solvent	time (h)	yield (%)[b]
1	Pd(OAc)$_2$/bpy	HOAc/THF/H$_2$O	24	trace
2	**A1**	CH$_3$NO$_2$	0.7	95
3	Pd(OAc)$_2$/bpy	CH$_3$NO$_2$	24	98
4	**A1**	dioxane	24	98
5	**A1**	DMSO	24	0
6	**A1**	DMF	24	trace
7	**A1**	HMPA	24	0
8	**A1**	toluene	24	0
9	**A1**	cyclohexane	24	0
10	**A1**	CH$_3$NO$_2$	0.7	98[c]

[a] Reaction conditions: PhB(OH)$_2$ (0.50 mmol), 4-nitrobenzaldehyde (0.25 mmol), cationic Pd(II) complex **A1** (2.5 mol %), CH$_3$NO$_2$ (0.5 mL) in a sealed tube at 80 °C. [b] Isolated yield. [c] PhB(OH)$_2$ (0.30 mmol, 1.2 equiv).

TABLE 2. Effect of the Counter Anions of Cationic Pd(II) Complexes and the Catalyst Loading[a]

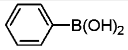
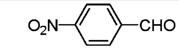
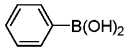
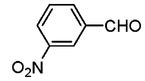
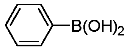
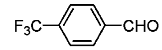
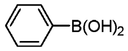
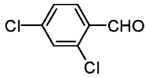
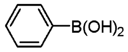
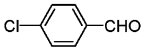
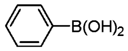
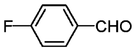
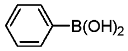
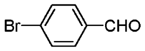
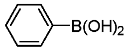
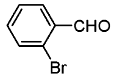
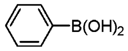
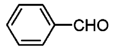
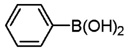
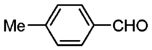
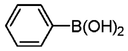
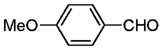
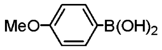
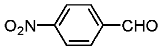
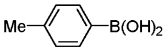
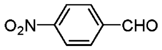
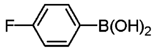
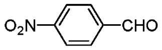
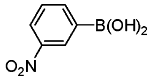
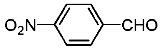
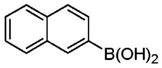
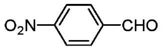
entry	anion, X$^-$	temp (ºC)	time (h)	yield (%)[b]
1	BF$_4^-$ (**A2**)	25	1.5	99
2	OTf$^-$ (**A1**)	25	4	87[c]
3	NO$_3^-$ (**A3**)	25	36	96
4	BF$_4^-$ (**A2**)	50	1	96
5	OTf$^-$ (**A1**)	50	3	99
6	NO$_3^-$ (**A3**)	50	24	96
7	BF$_4^-$ (**A2**)	50	10	99[d]
8	BF$_4^-$ (**A2**)	50	48	99[e]

[a] Reaction conditions: PhB(OH)$_2$ (0.12 mmol), 4-nitrobenzaldehyde (0.10 mmol), cationic Pd(II) complex (0.0025 mmol, 2.5 mol %), CH$_3$NO$_2$ (0.3 mL) in a sealed tube. [b] Isolated yield. [c] The yield was not increased for a longer reaction time. [d] PhB(OH)$_2$ (0.60 mmol), 4-nitrobenzaldehyde (0.50 mmol), cationic Pd(II) complex **A2** (0.5 mol %). [e] PhB(OH)$_2$ (1.2 mmol), 4-nitrobenzaldehyde (1.0 mmol), cationic Pd(II) complex **A2** (0.25 mol %).

groups.[9a,c−f] To the best of our knowledge, only a few works[10] were reported with use of Pd catalyst for this reaction. Herein, we wish to report the cationic Pd(II)/bpy-catalyzed addition of arylboronic acids to aldehydes.

First, we tried the addition of phenylboronic acid to 4-nitrobenzaldehyde using our previously reported optimized conditions for conjugate addition. Only trace amounts of the desired product **1** were detected (Table 1, entry 1). The success of the catalysis of cationic Pd(II) complex **A1** with bpy ligands for the addition of arylboronic acids to nitriles[8a] prompted us to use **A1** as the catalyst for this reaction. To our surprise, 95% of the addition product **1** was isolated in CH$_3$NO$_2$ at 80 °C after 40 min (Table 1, entry 2). When the neutral palladium catalyst was used in CH$_3$NO$_2$, the reaction also afforded **1** in 98% yield but a prolonged time was required (Table 1, entry 3). The reaction rate was slower when the reaction was carried out in dioxane, but 98% yield of product was still obtained after 24 h (Table 1, entry 4). In the other polar solvents such as DMSO, DMF, and HMPA, and nonpolar solvents such as toluene and cyclohexane, the reaction can hardly proceed (Table 1, entries 5−9). The cationic Pd(II) complex **A1** is insoluble in nonpolar solvent, and the polar solvent molecules with high coordinating ability might occupy the vacant coordination site of cationic Pd(II) complexes. Thus, CH$_3$NO$_2$ is the better choice as the solvent. The nearly quantitative yield was still maintained when the amount of phenylboronic acid was decreased to 1.2 equiv (Table 1, entry 10).

TABLE 3. Cationic Pd(II) Complex A2-Catalyzed Addtion of Arylboronic Acids to Aldehydes[a]

entry	ArB(OH)$_2$	aldehyde	time (h)	yield (%)[b]	
1			10	**1**	99
2			10	**2**	94
3			8	**3**	90
4			10	**4**	99
5			10	**5**	96
6			10	**6**	78
7			10	**7**	62
8			10	**8**	92
9			24	**9**	60
10			24	**10**	43
11[c]			5	**11**	14
12[d]			1	**12**	99
13			10	**13**	99
14			10	**14**	99
15			24	**15**	93
16			48	**16**	68

[a] Reaction conditions: ArB(OH)$_2$ (0.60 mmol), aldehyde (0.50 mmol), cationic Pd(II) complex **A2** (0.5 mol %), CH$_3$NO$_2$ (0.3 mL), 50 °C. [b] Isolated yield. [c] 2.5 mol % of Pd catalyst **A2** at 25 °C, prolonged time made the reaction disordered. [d] 2.5 mol % of Pd catalyst **A2**, room temperature.

The effect of different counter anoins of Pd(II) complexes was also examined. With BF$_4^-$ as the anion, the reaction was completed at room temperature in 1.5 h affording 99% yield (Table 2, entry 1). For OTf$^-$, the aldehyde could not be completely converted at room temperature (Table 2, entry 2). As for NO$_3^-$, the yield was also excellent but the rate was slower (Table 2, entry 3). Higher temperature sped up the reaction and

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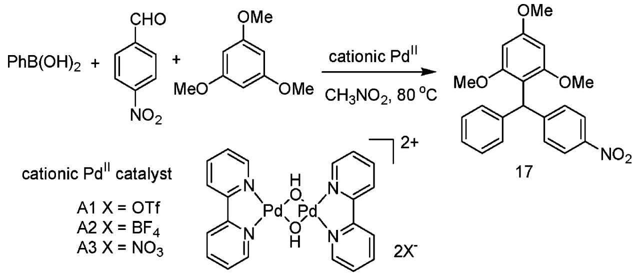
[10] (a) Yamamoto, T.; Ohta, T.; Ito, Y. *Org. Lett.* **2005**, *7*, 4153. (b) Suzuki, K.; Arao, T.; Ishii, S.; Maeda, Y.; Kondo, K.; Aoyama, T. *Tetrahedron Lett.* **2006**, *47*, 5789. (c) He, P.; Lu, Y.; Dong, C.-G.; Hu, Q.-S. *Org. Lett.* **2007**, *9*, 343. (d) During the preparation of this manuscript, we found: Qin, C.; Wu, H.; Cheng, J.; Chen, X.; Liu, M.; Zhang, W.; Su, W.; Ding, J. *J. Org. Chem.* **2007**, *72*, 4102.

TABLE 4. Condition Optimization of the One-Pot Synthesis of Unsymmetrical Triarylmethanes[a]



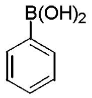
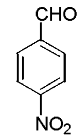
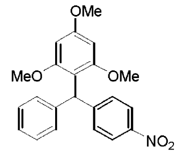
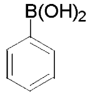
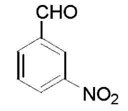
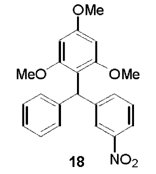
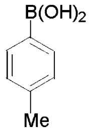
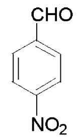
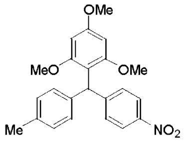
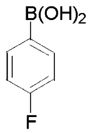
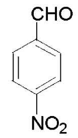
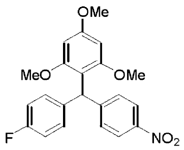
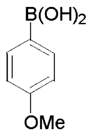
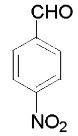
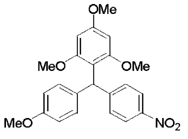
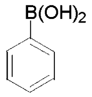
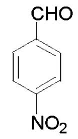
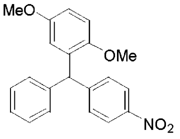
entry	arene/aldehyde (molar ratio)	anion X$^-$	time (h)	yield (%)[c]
1[b]	1.0	OTf$^-$ (**A1**)	8	21[d]
2	1.0	OTf$^-$ (**A1**)	4	40[d]
3	1.0	OTf$^-$ (**A1**)	24	52
4	1.0	OTf$^-$ (**A1**)	24	40[e]
5	1.0	OTf$^-$ (**A1**)	24	trace[f]
6	2.0	OTf$^-$ (**A1**)	24	84
7	2.0	NO_3^- (**A3**)	24	40
8	2.0	BF_4^- (**A2**)	24	92
9	2.0	BF_4^- (**A2**)	24	96[g]

[a] Reaction conditions: PhB(OH)$_2$ (0.20 mmol), aldehyde (0.10 mmol), 1,3,5-trimethoxybenzene, cationic Pd(II) complex (2.5 mol %), CH_3NO_2 (0.3 mL), 80 °C. [b] Reaction conditions: PhB(OH)$_2$ (0.20 mmol), aldehyde (0.10 mmol), cationic Pd(II) complex (2.5 mol %), and CH_3NO_2 (0.3 mL) were first reacted at 80 °C, 1,3,5-trimethoxybenzene was added after the completion of the first step. [c] Isolated yield. [d] The yield was not increased for a longer reaction time. [e] Addition of 3 Å MS (10 mg). [f] Addition of H_2O (0.05 mL). [g] PhB(OH)$_2$ (0.12 mmol).

the yields were excellent (Table 2, entries 4−6). Thus BF_4^- was chosen as the optimized anion. Cationic Pd(II) complex **A2** is highly effective for addition of arylboronic acids to aldehydes. Nearly quantitative yields were still maintained even when the catalyst loading was decreased to 0.5 or 0.25 mol % (Table 2, entries 7 and 8). Thus, PhB(OH)$_2$ (0.60 mmol), aldehyde (0.50 mmol), cationic Pd(II) complex **A2** (0.0025 mmol, 0.5 mol %), and CH_3NO_2 (0.3 mL) in a sealed tube at 50 °C were chosen as the optimized conditions.

The scope of the reaction with different aromatic aldehydes is outlined in Table 3. For aldehydes with electron-withdrawing groups, good to nearly quantitative yields were obtained (Table 3, entries 1−8). While the electron-withdrawing groups (e.g., nitro-, chloro-, and bromo-substituents) of arylaldehydes are not tolerated in the reaction with Grignard reagents or the organolithium reagents,[11] the tolerance of these electron-withdrawing groups is the advantage of this reaction. When benzaldehyde and electron-donating aldehydes were used in the reaction, the yields dropped (Table 3, entries 9 and 10). For anisaldehyde, the reaction was disordered at 50 °C. When 2.5 mol % of Pd(II) catalyst was loaded at room temperature, only 14% of desired product was isolated after 5 h (Table 3, entry 11). Also the influence of different arylboronic acids was examined. The reaction of *p*-methoxyphenylboronic acid in 50 °C also gave a mixture of products, but the reaction afforded nearly quantitative yield of addition product after 1 h when 2.5 mol % of Pd(II) catalyst **A2** was loaded at room temperature (Table 3, entry 12). For the other arylboronic acids tested, good to excellent yields of addition products were isolated (Table 3, entries 13−16).

TABLE 5. Cationic Pd(II) Complex A2-Catalyzed One-Pot Synthesis of Unsymmetrical Triarylmethanes[a]

entry	ArB(OH)$_2$	ArCHO	product	yield (%)[b]
1			 **17**	96
2			 **18**	79
3			 **19**	92
4			 **20**	78
5			 **21**	99
6			 **22**	57[c]

[a] Reaction conditions: ArB(OH)$_2$ (0.12 mmol), ArCHO (0.10 mmol), 1,3,5-trimethoxybenzene (0.20 mmol), cationic Pd(II) complex **A2** (2.5 mol %), CH_3NO_2 (0.3 mL), 80 °C. [b] Isolated yield. [c] 1,4-Dimethoxybenzene (0.20 mmol) was used as the third component.

A plausible mechanism for the cationic palladium-catalyzed addition of arylboronic acids to arylaldehydes is shown in Scheme 1. First, transmetalation between arylboronic acid and palladium catalyst yields the arylpalladium species **I**, followed by the coordination of the arylaldehyde giving **II**. Addition of the carbon−palladium bond to the carbonyl group yields diarylmethoxypalladium species **III**. Transmetalation of **III** with arylboronic acid followed by protonolysis gives the addition product and regenerates the species **I**.[9f] With these results in hand, a new application of this reaction was tried. When PhB(OH)$_2$, 4-nitrobenzaldehyde, and 1,3,5-trimethoxybenzene were mixed in above standard conditions, an unsymmetrical triarylmethane, (*p*-nitrophenyl)-(2,4,6-trimethoxyphenyl)phenylmethane (**17**), was isolated in 21% yield. In the well-studied Lewis acid-catalyzed Friedel−Crafts addition of electron-rich arenes to aldehydes or imines, symmetrical triarylmethanes were generally produced,[12a−h] but few examples of one-pot synthesis of

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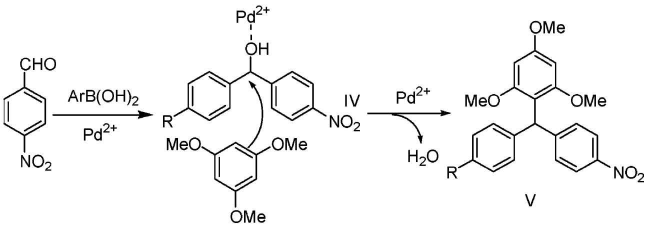
[11] Larock, R. C. *Comprehensive Organic Transformations*: *A Guide to Functional Preparations,* 2nd ed.; Wiley-VCH: New York, 1999.

SCHEME 2. Possible Pathway of the Formation of Unsymmetrical Triarylmethanes



unsymmetrical triarylmethanes were reported.[12e] In our reaction, a molecule containing three kinds of aryl rings with different electronic characteristics can be constructed in one pot. Inspired by this result, we began to survey the reaction conditions. The optimization results are summarized in Table 4.

Our strategy of optimization was to carry this reaction in one pot with two steps. 1,3,5-Trimethoxybenzene was added after $PhB(OH)_2$ reacted with aldehyde completely in half an hour. After 4 h, 40% of triarylmethane was obtained, and prolonged time gave higher yields (Table 4, entries 2 and 3). While the addition of water stopped the reaction completely (Table 4, entry 5), the addition of 3 Å MS did not help the reaction (Table 4, entry 4). Then 2.0 equiv of 1,3,5-trimethoxybenzene was added and the yield was improved to 84% (Table 4, entry 6). For different anions of Pd(II) catalysts, the catalyst with the BF_4^- as anion was proved to be the best (Table 4, entry 8). When the $PhB(OH)_2$ was decreased to 1.2 equiv, 96% yield of the product was isolated (Table 4, entry 9).

The results of different arylboronic acids and arylaldehydes are summarized in Table 5. It was shown that aryl groups with different electron density of arylboronic acids can be easily introduced with moderate to excellent yields (Table 5, entries 1−4). Arylboronic acid with electron-donating groups afforded the highest yield (Table 5, entry 5). Electron-deficient aldehydes were chosen for their high reactivity. As for electron-rich arenes, 1,3,5-trimethoxybenzene and 1,4-dimethoxybenzene (Table 5, entry 6) were the appropriate components. Other kinds of arenes, such as indoles and furans, often lead to complicated results. When anisole was used in the optimized conditions, no reaction occurred.

The formation of unsymmetrical triarylmethanes may proceed via the following pathway (Scheme 2).[12e] First, arylboronic acids were added to the carbonyl group of the aldehydes, and diarylmethanol **IV** was formed. Then, the hydroxy group of intermediate **IV** was activated by the cationic Pd(II) species and the electron-rich arene was added to **IV** to yield triarylmethane **V**.

In conclusion, we developed a cationic Pd(II)/bpy-catalyzed addition of arylboronic acids to aldehydes with low catalyst loading and high yields in mild conditions. A molecule containing three kinds of aryl rings with different electron density can be constructed in one pot and a convenient synthesis of unsymmetrical triarylmethanes was developed.

Experimental Section

General. All solvents were dried and distilled before use according to the standard methods. All melting points were uncorrected.

Procedure for the Addition of Phenylboronic Acid to 4-Nitrobenzaldehyde. Phenylboronic acid (73 mg, 0.60 mmol), 4-nitrobenzaldehyde (76 mg, 0.50 mmol), cationic Pd(II) complex **A2** (1.7 mg, 0.0025 mmol, 0.5 mol %), and CH_3NO_2 (0.4 mL) were mixed in a sealed tube. The tube was sealed and the mixture was stirred and heated at 50 °C for 10 h until the substrate disappeared as monitored by TLC. The reaction mixture was concentrated under reduced pressure. The residue was purified by flash chromatography (EtOAc:petroleum ether 1:5) to give the product **1** (114 mg, 0.50 mmol) with 99% yield as a light yellow oil.[13] Mp 70−71 °C (lit.[13] mp 72 °C); ^1H NMR (300 MHz, $CDCl_3$) δ 8.20 (d, $J = 8.7$ Hz, 2H), 7.59 (d, $J = 8.7$ Hz, 2H), 7.41−7.29 (m, 5H), 5.93 (d, $J = 3.3$ Hz, 1H), 2.38 (d, $J = 3.3$ Hz, 1H); IR (KBr) ν 3500, 1596, 1515, 1344, 707 cm^{-1}; MS (70 eV, EI) m/z (%) 229 (M^+), 150, 105, 79, 44 (100).

Procedure for the Synthesis of (*p*-Nitrophenyl)(phenyl)(2,4,6-trimethoxyphenyl)methane (17). Phenylboronic acid (15 mg, 0.12 mmol), 4-nitrobenzaldehyde (15 mg, 0.10 mmol), cationic Pd(II) complex **A2** (1.7 mg, 0.0025 mmol, 5 mol %), and CH_3NO_2 (0.3 mL) were mixed in a sealed tube. The tube was sealed and the mixture was stirred and heated at 80 °C for 0.5 h until the substrates disappeared as monitored by TLC. Then 1,3,5-trimethoxybenzene (34 mg, 0.20 mmol) was added and the tube was sealed and heated for 24 h. The reaction mixture was concentrated under reduced pressure. The residue was purified by flash chromatography (EtOAc:petroleum ether 1:10) to give the product **17** (36 mg, 0.096 mmol) with 96% yield as a light yellow solid. Mp 97−98 °C; ^1H NMR (300 MHz, $CDCl_3$) δ 8.11−8.02 (m, 2H), 7.34−7.15 (m, 7H), 6.15 (s, 2H), 6.09 (s, 1H), 3.81 (s, 3H), 3.61 (s, 6H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 160.5, 158.8, 153.1, 145.7, 142.0, 129.5, 129.1, 128.0, 126.1, 122.7, 111.7, 91.3, 55.5, 55.3, 45.2; IR (KBr) ν 2935, 2839, 1605, 1593, 1515, 1452, 1345, 1224, 1114, 812, 701 cm^{-1}; MS (70 eV, EI) m/z (%) 380 ($M^+ + 1$), 379 (M^+, 100), 302, 257, 149, 91, 71, 43. HRMS calcd for $C_{22}H_{21}NO_5$ 379.1420, found 379.1420.

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Supporting Information Available: Typical experimental procedure and characterization data of all products. This material is available free of charge via the Internet at http://pubs.acs.org.

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