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Palladium Catalyzed Double Suzuki-Miyaura Reactions Using Cyclic Dibenziodoniums: Synthesis of *ortho*-Tetraaryls

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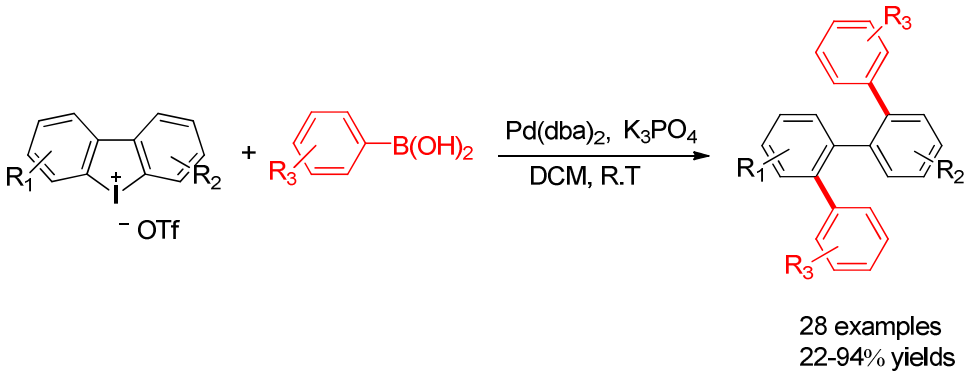


Abstract

Palladium catalyzed double Suzuki-Miyaura couplings between cyclic dibenziodoniums and arylboronic acids have been developed. As such, a wide range

of *ortho*-tetraaryls were synthesized in good to excellent yields of 22-94%. Furthermore, tetraphenylene was prepared in 21% isolated yield with 2,2'-biphenyldiboronic acid by using this method.

Introduction

ortho-tetraaryls are advantageous building blocks for the construction of specific polyaromatic hydrocarbons (PAHs)[1], which were now well-established as functional materials (**A-B**, Figure 1)[2] or catalyst ligands (**C**, Figure 1).[3] Furthermore, *ortho*-oligoaryls were identified to adopt a helical conformation, leading to applications as three-dimensional scaffolds in the study of steric interactions along the rigid backbone.[4] With regard to the preparation of *ortho*-oligoaryls, mono-Suzuki-Miyaura couplings between the biphenyl derivatives are well recorded (1. Mono-coupling, Figure 1).[5] however, the availability of starting materials is very limited. On the other hand, double coupling reaction is very versatile and thus therefore generally employed in the synthesis of polyaromatic compounds.[6] In this context, double Suzuki-Miyaura couplings between dihaloaryls and two molecules of arylboric acids, or diboron compounds with two molecules of arylhalogens, have been reported.[7] Surprisingly, dihalobiphenyls as Suzuki-Miyaura coupling parters were rarely studied. López-Romero employed *p*-dibromobiphenyl derivatives in coupling reactions; but mono-coupling products were preferentially obtained.[8] Very recently, Li and Wang reported double cross coupling reaction of

2,2'-dibromobiphenyls with 1,1-diboronates, 9*H*-fluorenes were synthesized in excellent yields.[9]

Five-membered cyclic iodonium salts, belong to a class of hypervalent iodoniums, are particularly interesting because of their stability and numerous applications in biological studies.[10] For example, diphenyleneiodonium chloride (DPI) has found to be a specific inhibitor for the activity of flavoenzymes. Whereas, being environmentally benign reactants in organic synthesis, cyclic dibenziodonium salts have been long-term ignored until recent reports described the activation of C-I bonds in multi-component cascade reactions.[11] In connection with our continued interests in exploring reactivity of hypervalent iodine reagents for multi-arylations,[12] herein we reported palladium catalyzed double Suzuki-Miyaura coupling reaction by using dibenziodoniums for the synthesis of *ortho*-tetraaryls (2, Figure 1).

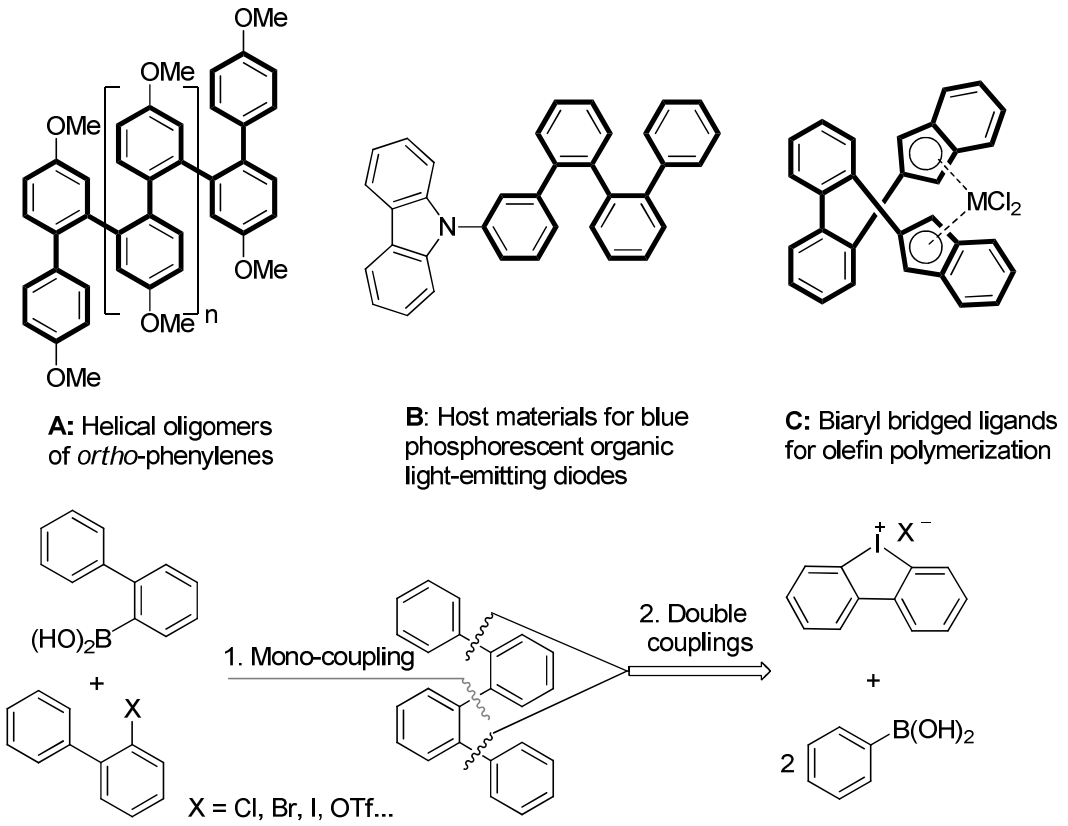


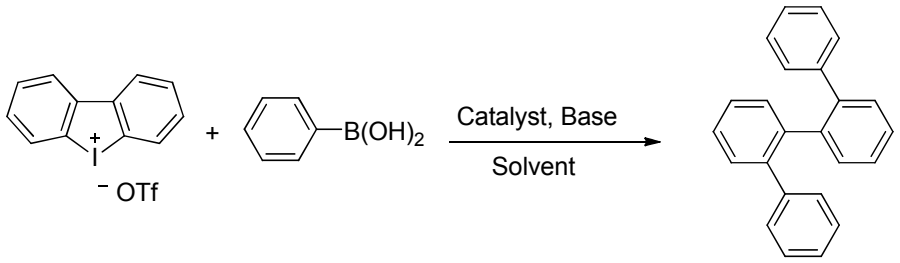
Figure 1. Selective examples of *ortho*-tetraaryl derivatives and two of the possible disconnections for *ortho*-tetraphenyls.

Results and Discussion

Our investigation began with an examination of the coupling of cyclic iodonium salt **1a** with phenyl boronic acid **2a** in the presence of palladium catalysts, various inorganic bases and a mixture of acetone/water as a solvent. $Pd(dba)_2$ was found to be the suitable catalyst, and K_3PO_4 was the optimal base to furnish the desired product **3aa** in 65% yield after 12 hours (entries 1-6, Table 1). Afterwards, various solvents were screened in the reaction, and the use of dichloromethane generated the product in 67% yield at room temperature. Fortuitously, we found that variations in the amount of K_3PO_4

markedly influenced the yield of **3aa**, an increased loading of K_3PO_4 (5 equiv.) lead to an excellent yield of 84% of **3aa**. To our delight, the reaction proceeded efficiently at a lower catalytic loading of 1 mol% $Pd(dba)_2$ and afforded **3aa** in 92% yield (entry 15, Table 1). Notably, under the optimized reaction conditions, 2,2'-diiodobiphenyl was employed for replacement of iodonium **1a**, *ortho*-tetraphenyl **3aa** were obtained in a moderate yield of 32%, a large amount of diphenyls was isolated. The formation of diphenyls was ascribed to both deiodination of 2,2'-diiodobiphenyls and homocoupling of phenyl boronic acids (entry 16, Table 1).

Table 1. Screening of reaction conditions for double Suzuki– Miyaura reaction.[a]



1a **2a** **3aa**

Entry	Catalyst	Base	Equiv. of bases	Solvent	% yield[c]
1[b]	$Pd(OAc)_2$	K_3PO_4	3.0	Acetone/H_2O	43
2[b]	$Pd(BINAP)_2Cl_2$	K_3PO_4	3.0	Acetone/H_2O	34
3[b]	$Pd(dba)_2$	K_3PO_4	3.0	Acetone/H_2O	49
4	$Pd(dba)_2$	K_3PO_4	3.0	Acetone/H_2O	65
5	$Pd(dba)_2$	KOH	3.0	Acetone/H_2O	33
6	$Pd(dba)_2$	KF	3.0	Acetone/H_2O	11
7	$Pd(dba)_2$	K_3PO_4	3.0	THF	43

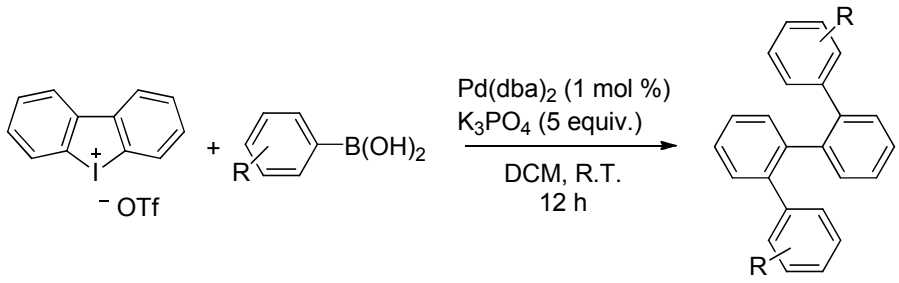
8	$Pd(dba)_2$	K_3PO_4	3.0	toluene	64
9	$Pd(dba)_2$	K_3PO_4	3.0	^{i}PrOH	49
10	$Pd(dba)_2$	K_3PO_4	3.0	H_2O	36
11	$Pd(dba)_2$	K_3PO_4	3.0	DCM	67
12	$Pd(dba)_2$	K_3PO_4	3.0	DCE	65
13	$Pd(dba)_2$	K_3PO_4	4.0	DCM	78
14	$Pd(dba)_2$	K_3PO_4	5.0	DCM	84
15 [d]	$Pd(dba)_2$	K_3PO_4	5.0	DCM	92
16 [f]	$Pd(dba)_2$	K_3PO_4	5.0	DCM	32

[a]Unless otherwise specified, reaction conditions: **1a** (0.2 mmol), **2a** (0.44 mmol), catalyst (10 mol %), base and 4.4 mL solvent; room temperature, 12 hours. [b]Reaction time is 5 hours. [c]Isolated yield. [d]Catalyst loading was 1 mol %. [f]2,2'-Diiodobiphenyl was used in place of **1a** .

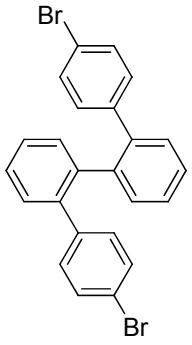
With the optimal conditions established, we subsequently examined the substrate scope of aryl boronic acids to test the feasibility of preparing a variety of *ortho*-tetraaryls. The results were summarized in Table 2. Generally, aryl boronic acids bearing various substituents of halogens, methoxy, phenyl, cyano, nitro, trifluoromethyl or methyl groups regardless of their electronic nature, are well tolerated in the reactions. 4-Methoxyphenylboronic acid (**2n**) gave **3an** in the highest yield of 94%, suggesting electron-donating substituents in favor of the reaction efficiency (**3an** *vs* **3ad**, **3ae**; Table 2). 3-Nitrophenylboronic acid gave a very low yield of 22% (**3am**). Furthermore, the substituents on the *ortho*-, *meta*- or *para*- positions of phenyl ring of boronic acids were employed. The results suggested that the steric effect on the reaction yields are depended on the substituent employed. For example,

4-chlorophenylboronic acid (**2i**) gave the desired product more efficiently than 2-chlorophenylboronic acid (**3ai** *vs* **3ag**); however, 2-methylphenylboronic acid (**2k**) afforded the higher yield than 4-methylphenylboronic acid (**2j**). 2-Methoxybenzeneboronic acid (**2o**) afforded **3ao** in a moderate yield of 43%. Disubstituted phenyl boronic acid (**2f**) furnished **3af** in 84% yield. 2-Naphthaleneboronic acid and 4-biphenylboronic acid worked well in this double coupling reaction, the desired product **3ap** was obtained in 92% yield and **3aq** was obtained in 80% yield, respectively. Fortunately, heterocyclic boronic acids such as *2*-furanylboronic acid and 3-thienylboronic acid can transfer the heterocycles into the desired tetraaryls albeit in a moderate yields of 27% and 45%, respectively (**3ar** and **3as**, Table 2). However, 4-pyridylboronic acid resulted in no product at all.

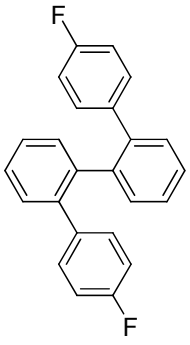
Table 2. Scope of diverse aryl boronic acids in Suzuki reactions. [a,b]



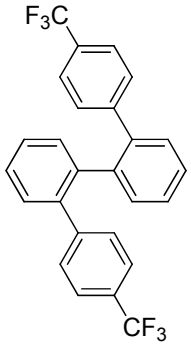
1a **2** **3**



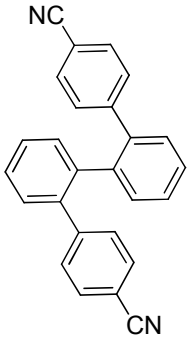
3ab, 88%



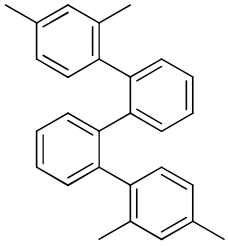
3ac, 59%



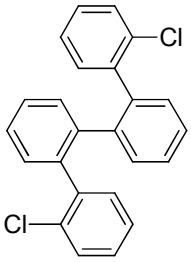
3ad, 62%



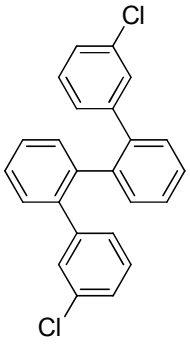
3ae, 66%



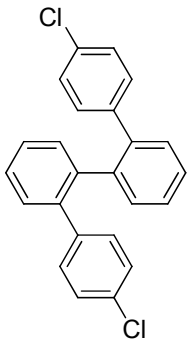
3af, 84%



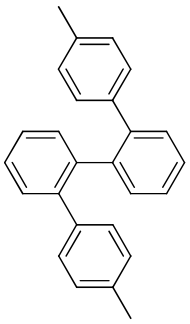
3ag, 65%



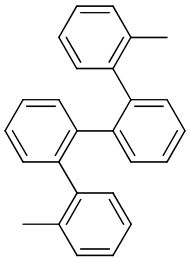
3ah, 89%



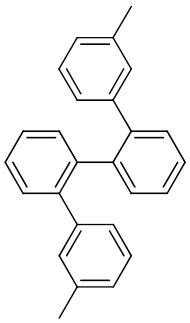
3ai, 91%



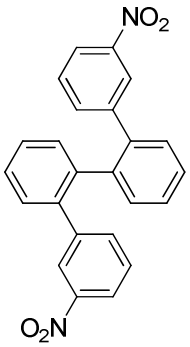
3aj, 83%



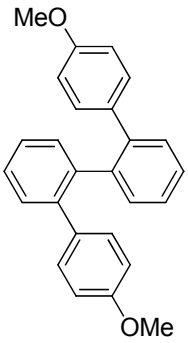
3ak, 91%



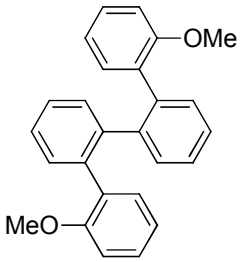
3al, 76%



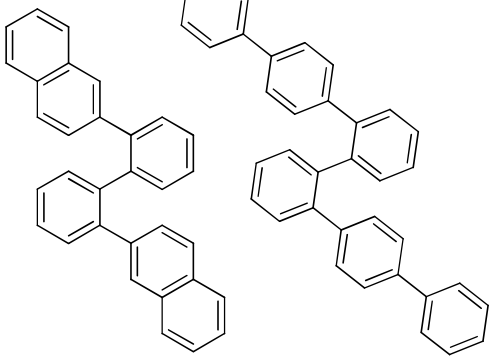
3am, 22%



3an, 94%

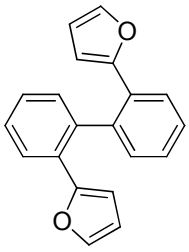


3ao, 43%

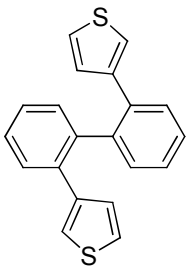


3ap, 92%

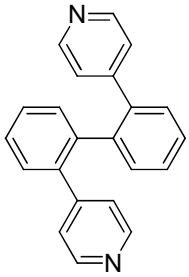
3aq, 80%



3ar, 27%



3as,45%



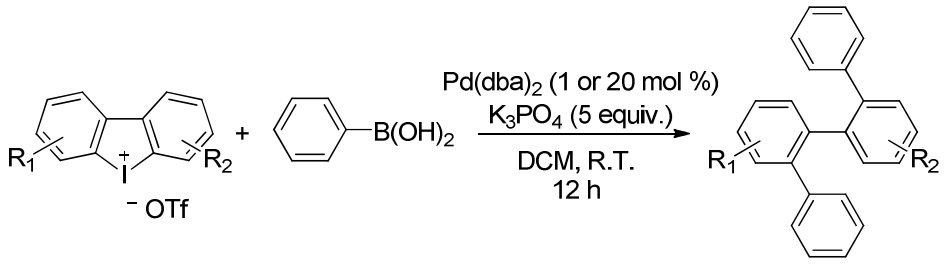
3at, 0%

[a]Unless otherwise specified, reaction conditions: **1a** (0.2 mmol), **2** (0.44 mmol), $Pd(dba)_2$ (1 mol %), K_3PO_4 (1.0 mmol) in 4.4 mL DCM; room temperature, 12 hours. [b]Isolated yield.

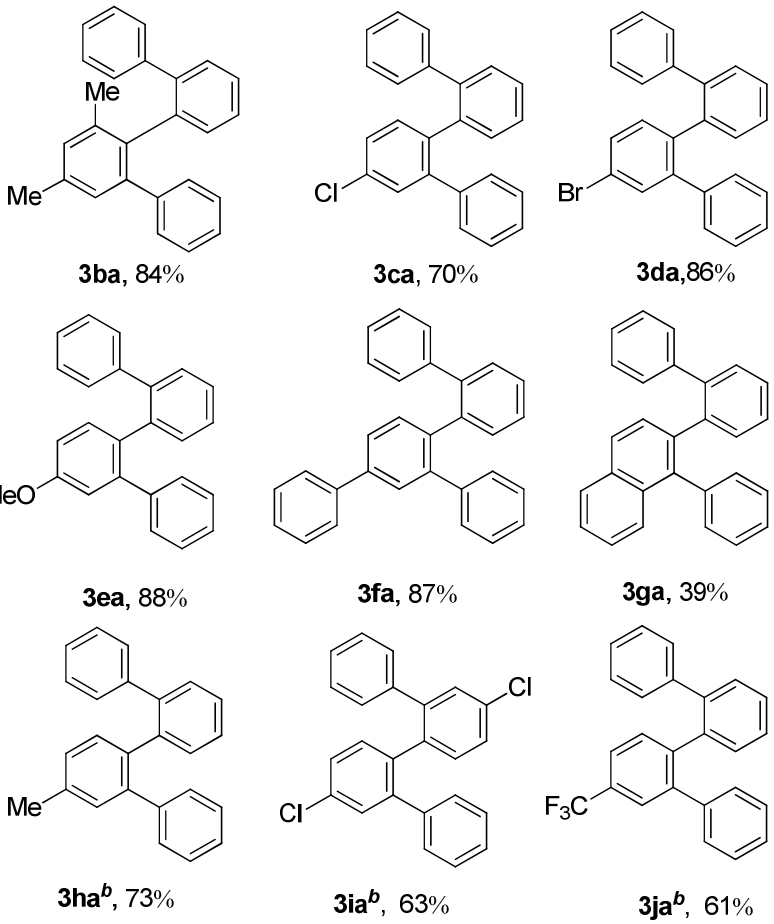
Next, we turned our attention to the scope of cyclic dibenziodonium as coupling partners. As demonstrated in Table 3, a variety of unsymmetrical cyclic diphenyleneiodoniums were empolyed to assess substitution effect on

the reactivity. In general, the iodonium salts with various substitutions generated the structural diversity of *ortho*-tetraaryls (**3ba**-**3ja**), which demonstrated the generality of this double cross coupling reactions. Surprisingly, when iodonium salts **1h, 1i** and **1j** were employed in the reaction, 20 mol% palladium catalyst was necessary for an efficient conversion (73% yield of **3ha**, 63% yield of **3ia**, 61% yield of **3ja**), the standard catalyst loading of 1 mol% $Pd(dba)_2$ only gave less than 10% yield of desired products after a long reaction time of 24 hours.

Table 3. Scope of the cyclic dibenziodoniums in Suzuki reactions.[a,c]



1 **2a** **3**



3ba, 84% **3ca**, 70% **3da**, 86%

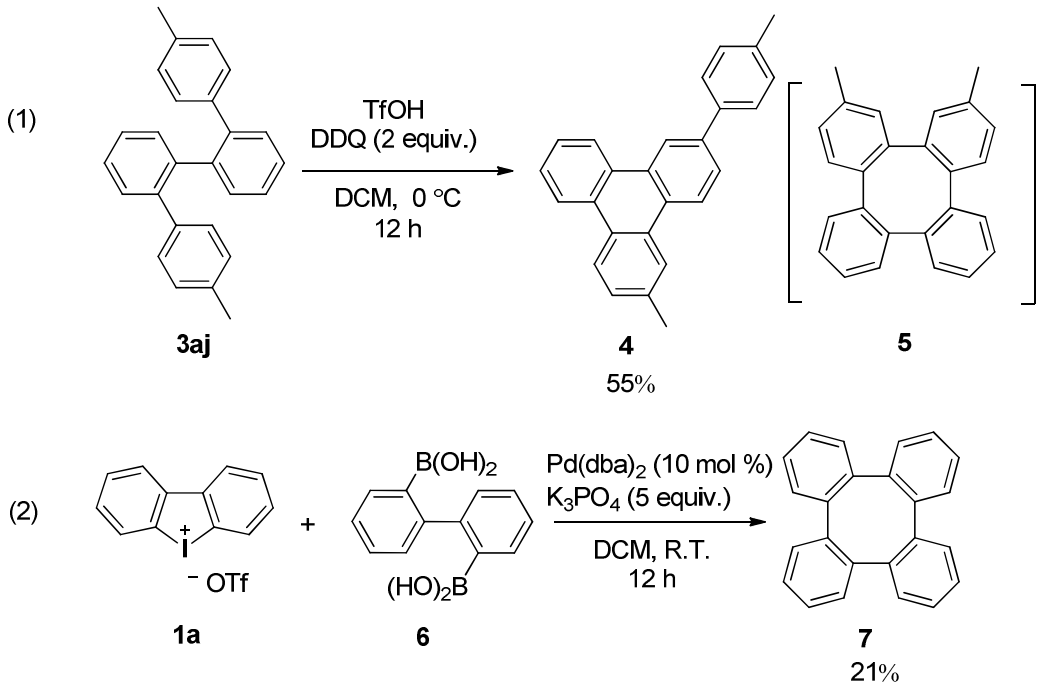
3ea, 88% **3fa**, 87% **3ga**, 39%

3ha[b], 73% **3ia**[b], 63% **3ja**[b], 61%

[a]Unless otherwise specified, reaction conditions: **1** (0.2 mmol), **2a** (0.44 mmol), $Pd(dba)_2$ (1 mol %), K_3PO_4 (1.0 mmol) in 4.4 mL DCM; room temperature, 12 hours. [b]$Pd(dba)_2$ (20 mol %). [c]Isolated yield.

To explore the reaction scope for potential utility, we wished to produce tetraphenylene derivatives which are well studied by H. N. C. Wong.[13] We then chose product of **3aj** for a further intramolecular dehydrogenative coupling reaction (Scholl reaction) to test the possibility of preparation of tetraphenylene of **5** ((1), Scheme 1.). Unfortunately, the Scholl reaction gave the coupling product of **4** but not **5** according to the ^1H NMR spectra (see the Supporting Information).[2g] Inspired by our recent report on palladium catalyzed double

Suzuki reaction toward tetraphenylenes,[14] we chose **1a** and 2,2'-biphenyldiboronic acid **6** in the direct double Suzuki-Miyaura reaction. As expected, tetraphenylene **7** was obtained in 21% yield under the standard conditions ((2), Scheme 1.). Obviously, this method provides an alternative to prepare specific tetraphenylene derivatives.



Scheme 1. Double coupling reactions towards tetraphenylenes; DDQ = 2,3-dichloro-5,6-dicyano-1,4-benzoquinone.

Conclusion

In summary, we have developed a method of double Suzuki-Miyaura coupling reaction between cyclic dibenziodonium salts and arylboronic acids in the presence of palladium catalyst. As such, a wide range of *ortho*-tetraaryls was

synthesized in good to excellent yields of 22-94%. It is anticipated that some useful molecules of PAHs could be produced by this method in the future.

Experimental Section

General Methods. The cyclic dibenziodoniums were prepared according to the literature.[10, 11c] Unless otherwise stated, all reactions were performed under an atmosphere of air. Commercially available reagents were used without further purification. ^{1}H and ^{13}C NMR spectra were recorded at 400 MHz spectrometer. ^{1}H and ^{13}C NMR spectra were referenced internally to residual protio-solvent (^{1}H) or solvent (^{13}C) resonances and are reported relative to tetramethylsilane. Chemical shifts are reported in ppm from tetramethylsilane. Data are reported as follows: brs = broad singlet, s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet; coupling constants in Hz. LRMS and HRMS were measured in EI mode, High resolution mass spectra (HRMS) was measured in a TOF mass spectrometer. Column chromatography was performed on silica gel (300-400 mesh). Melting points were determined in open capillaries and are uncorrected.

General Procedure for the synthesis of 3aa-3at

Aryl boronic acid **2** (0.44 mmol, 2.2 eq.), $Pd(dba)_2$ (1.15 mg, 0.002 mmol, 1 mol %) were added to a reaction tube. Then 2 mL DCM was added using a syringe. The reaction mixture was stirred for 15 min, then cyclic dibenziodoniums **1a** (85.6 mg, 0.2 mmol, 1.0 eq.) and anhydrous K_3PO_4 (212.3 mg, 1.0 mmol, 5.0 eq.) in 2.4 mL DCM were added. The reaction was stirred at room temperature for 12 hours. After the solvent was removed in *vacuo* and the residue was purified by silica gel using eluents

(hexane) to afford the desired products except for **3ae**, **3am**, **3an**, **3ao** (using a mixture eluents of hexane/ ethyl acetate).

2,2'-Bis(phenyl)biphenyl (3aa).[15] The crude product was purified by flash chromatography (hexane) to obtain **3aa** (white solid, 56.3 mg, 92% yield). M. p.: 117-122 ˚C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.48-7.41 (m, 2H), 7.41-7.30 (m, 4H), 7.24-7.16 (m, 2H), 7.10 (t, J = 6.8 Hz, 2H), 7.02 (t, J = 7.2 Hz, 4H), 6.64 (d, J = 6.8 Hz, 4H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 141.0, 140.9, 140.0, 131.7, 129.9, 129.3, 127.46, 127.42, 127.1, 125.9; MS (EI): m/z (%) 306 (M^+, 100).

2,2'-Bis(4-bromophenyl)biphenyl (3ab).[16] The crude product was purified by flash chromatography (hexane) to obtain **3ab** (white solid, 81.7 mg, 88% yield). M. p.: 182-184 ˚C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.47-7.31 (m, 6H), 7.15-7.06 (m, 6H), 6.44-6.37 (m, 4H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 139.7, 139.6, 139.5, 131.7, 130.7, 130.6, 129.7, 127.9, 127.7, 120.4; MS (EI): m/z (%) 464 (M^+, 100), 304 (81), 152 (67), 228 (31).

2,2'-Bis(4-fluorophenyl)biphenyl (3ac). The crude product was purified by flash chromatography (hexane) to obtain **3ac** (white solid, 42.4 mg, 59% yield). M. p.: 164-167 ˚C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.47-7.42 (m, 2H), 7.39 (td, J = 7.2, 1.2 Hz, 2H), 7.34 (td, J = 7.6, 1.6 Hz, 2H), 7.11 (dd, J = 7.6, 1.2 Hz, 2H), 6.69 (t, J = 8.8 Hz, 4H), 6.55-6.48 (m, 4H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 161.5 (d, J = 244.0 Hz), 139.8, 136.8 (d, J = 3.1 Hz), 131.6, 130.57 (d, J = 8.0 Hz), 129.8, 127.7, 127.4, 114.3 (d, J = 21.0 Hz); HRMS (EI) for $C_{24}H_{16}F_2$: calculated $[M]^+$, 342.1220. Found, 342.1218.

2,2'-Bis(4-trifluoromethylphenyl)biphenyl (3ad). The crude product was purified by flash chromatography (hexane) to obtain **3ad** (white solid, 54.9 mg, 62% yield). M. p.:

149-153 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.56-7.51 (m, 2H), 7.48 (td, J = 7.6, 0.8 Hz, 2H), 7.40 (td, J = 7.2, 1.2 Hz, 2H), 7.21 (d, J = 8.0 Hz, 4H), 7.17-7.12 (m, 2H), 6.58 (d, J = 8.0 Hz, 4H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 144.2, 139.5, 139.2, 131.9, 129.8, 129.2, 128.3, 128.1, 128.0, 124.4 (q, J = 4.0 Hz), 124.2 (q, J = 271.0 Hz); HRMS (EI) for $C_{26}H_{16}F_6$: calculated $[M]^+$, 442.1156. Found, 442.1162.

2,2'-Bis(4-cyanophenyl)biphenyl (3ae). The crude product was purified by flash chromatography (hexane/ethyl acetate = 20:1) to obtain **3ae** (white solid, 47.0 mg, 66% yield). M. p.: 304-308 °C.^{1}H NMR (400 MHz, CD_3COCD_3): δ 8.01 (d, J = 8.0 Hz, 3H), 7.73 (d, J = 8.0 Hz, 3H), 7.56-7.51 (m, 4H), 7.49-7.40 (m, 3H), 7.22 (d, J = 7.6 Hz, 1H), 6.73 (d, J = 8.4 Hz, 2H); ^{13}C NMR (100 MHz, CD_3COCD_3): δ 146.6, 140.6, 140.3, 135.9, 133.1, 132.7, 132.2, 131.1, 131.0, 130.0, 129.6, 119.8, 119.7, 114.8, 111.2; HRMS (EI) for $C_{26}H_{16}N_2$: calculated $[M]^+$, 356.1313. Found, 356.1309.

2,2'-Bis(2,4-dimethylphenyl)biphenyl (3af). The crude product was purified by flash chromatography (hexane) to obtain **3af** (white solid, 60.9 mg, 84% yield). M. p.: 112-115 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.58-7.15 (m, 6H), 7.10-6.50 (m, 8H), 2.37-2.18 (m, 6H), 1.67 (s, 3H), 1.33 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 141.1, 139.7, 137.5, 135.8, 131.9, 131.1, 130.8, 126.4, 126.3, 125.2, 21.0, 20.2, 19.5; HRMS (EI) for $C_{28}H_{26}$: calculated $[M]^+$, 362.2035. Found, 362.2029.

2,2'-Bis(2-chlorophenyl)biphenyl (3ag).[17] The crude product was purified by flash chromatography (hexane) to obtain **3ag** (white solid, 48.8 mg, 65% yield). M. p.: 136-139 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.62-7.27 (m, 6H), 7.25-6.72 (m, 10H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 140.2, 137.9, 133.8, 132.1, 131.4, 130.8, 129.6, 128.2,

127.3, 126.6, 126.1; MS (EI): m/z (%) 303 (100), 151 (66), 374 (M^+, 33), 339 (32), 226 (14).

2,2'-Bis(3-chlorophenyl)biphenyl (3ah). The crude product was purified by flash chromatography (hexane) to obtain **3ah** (white solid, 66.8 mg, 89% yield). M. p.: 97-100 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.51-7.47 (m, 2H), 7.43 (td, J = 7.2, 0.8 Hz, 2H), 7.37 (td, J = 7.2, 1.2 Hz, 2H), 7.13 (d, J = 7.6 Hz, 2H), 7.08 (d, J = 8.0 Hz, 2H), 6.91 (t, J = 8.0 Hz, 2H), 6.47 (s, 2H), 6.42 (d, J = 8.0 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 142.4, 139.6, 139.4, 133.5, 131.6, 131.5, 129.6, 129.1, 128.5, 127.9, 127.3, 126.1; HRMS (EI) for $C_{24}H_{16}Cl_2$: calculated $[M]^+$, 374.0629. Found, 374.0621.

2,2'-Bis(4-chlorophenyl)biphenyl (3ai). The crude product was purified by flash chromatography (hexane) to obtain **3ai** (white solid, 68.3 mg, 91% yield). M. p.: 161-164 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.48-7.43 (m, 2H), 7.41 (t, J = 7.6 Hz, 2H), 7.35 (t, J = 7.2 Hz, 2H), 7.12 (d, J = 7.2 Hz, 2H), 6.97 (d, J = 8.4 Hz, 4H), 6.49 (d, J = 8.4 Hz, 4H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 139.6, 139.2, 132.2, 131.6, 130.4, 129.7, 127.8, 127.7, 127.6; HRMS (EI) for $C_{24}H_{16}Cl_2$: calculated $[M]^+$, 374.0629. Found, 374.0634.

2,2'-Bis(4-methylphenyl)biphenyl (3aj). The crude product was purified by flash chromatography (hexane) to obtain **3aj** (white solid, 55.5 mg, 83% yield). M. p.: 133-135 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.35-7.26 (m, 6H), 7.20-7.14 (m, 2H), 6.82 (d, J = 8.0 Hz, 4H), 6.56 (d, J = 8.0 Hz, 4H), 2.26 (s, 6H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 140.9, 140.0, 138.1, 135.5, 131.6, 129.9, 129.1, 128.1, 127.3, 126.7, 21.0; HRMS (EI) for $C_{26}H_{22}$: calculated $[M]^+$, 334.1722. Found, 334.1721.

2,2'-Bis(2-methylphenyl)biphenyl (3ak).[18] The crude product was purified by flash chromatography (hexane) to obtain **3ak** (white solid, 60.9 mg, 91% yield). M. p.: 115-119 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.55-7.20 (m, 7H), 7.15-6.90 (m, 6H), 6.85 (t, J = 7.2 Hz, 2H), 6.76-6.65 (m, 1H), 1.67 (s, 3H), 1.37 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 140.9, 139.8, 136.5, 132.1, 131.9, 131.5, 130.7, 130.4, 126.6, 126.4, 126.3, 124.5, 20.3, 19.7; MS (EI): m/z (%) 334 (M^+, 100), 319 (30), 229 (13), 151 (13).

2,2'-Bis(3-methylphenyl)biphenyl (3al).[19] The crude product was purified by flash chromatography (hexane) to obtain **3al** (white solid, 50.8 mg, 76% yield). M. p.: 77-79 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.46-7.41 (m, 2H), 7.40-7.27 (m, 4H), 7.15 (dd, J = 7.6, 1.2 Hz, 2H), 6.91-6.82 (m, 4H), 6.41 (d, J = 6.8 Hz, 2H), 6.35 (s, 2H), 2.13 (s, 6H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 142.4, 141.0, 140.7, 140.1, 136.9, 131.5, 130.0, 129.7, 127.3, 126.9, 126.5, 126.4, 21.4; MS (EI): m/z (%) 334 (M^+, 100), 319 (22), 228 (19), 151 (16).

2,2'-Bis(3-nitrophenyl)biphenyl (3am). The crude product was purified by flash chromatography (hexane/ethyl acetate = 15:1) to obtain **3am** (white solid, 17.4 mg, 22% yield). M. p.: 194-197 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.96 (ddd, J = 8.4, 2.0, 0.8 Hz, 2H), 7.62-7.57 (m, 2H), 7.54 (td, J = 7.6, 1.2 Hz, 2H), 7.42 (td, J = 7.6, 1.2 Hz, 2H), 7.28 (t, J = 2.0 Hz, 2H), 7.16-7.08 (m, 4H), 6.82 (d, J = 8.0 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 147.7, 142.1, 139.1, 138.1, 134.9, 131.8, 129.7, 128.9, 128.6, 128.3, 123.9, 121.3; HRMS (EI) for $C_{24}H_{16}N_2O_4$: calculated $[M]^+$, 396.1110. Found, 396.1112.

2,2'-Bis(4-methoxyphenyl)biphenyl (3an).[20] The crude product was purified by flash chromatography (hexane/ethyl acetate = 60:1) to obtain **3an** (white solid, 68.9 mg, 94% yield). M. p.: 135-138 ˚C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.39-7.35 (m, 2H), 7.34-7.28 (m, 4H), 7.17-7.12 (m, 2H), 6.56 (s, 8H), 3.75 (s, 6H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 157.9, 140.5, 140.0, 133.6, 131.6, 130.2, 129.8, 127.3, 126.7, 112.9, 55.2; MS (EI): m/z (%) 366 (M^+, 100).

2,2'-Bis(2-methoxyphenyl)biphenyl (3ao). The crude product was purified by flash chromatography (hexane/ethyl acetate=100:1) to obtain **3ao** (colorless oil, 31.5 mg, 43% yield). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.30-7.10 (m, 10H), 6.75-6.55 (m, 6H), 3.42 (s, 6H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 156.3, 141.5, 137.3, 132.0, 131.5, 130.9, 130.4, 128.0, 126.5, 126.4, 120.1, 110.3, 54.8; HRMS (EI) for $C_{26}H_{22}O_2$: calculated $[M]^+$, 366.1620. Found, 366.1623.

2,2'-di(naphthalen-2-yl)-1,1'-biphenyl (3ap). The crude product was purified by flash chromatography (hexane) to obtain **3ap** (white solid, 74.8 mg, 92% yield). m. p.: 151-156 ˚C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.69 (d, J = 8.4 Hz, 2H), 7.56 (d, J = 7.6 Hz, 2H), 7.45-7.23 (m, 10H), 7.16 (t, J = 7.6 Hz, 4H), 6.73 (s, 2H), 6.63 (d, J = 8.4 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 141.0, 140.1, 138.5, 133.1, 131.7, 131.6, 130.1, 128.1, 128.0, 127.7, 127.4, 127.3, 127.2, 126.3, 125.5, 125.4; HRMS (EI) for $C_{32}H_{22}$: calculated $[M]^+$, 406.1722. Found, 406.1726.

4,4'''-diphenyl-o-quaterphenyl (3aq).[21] The crude product was purified by flash chromatography (hexane) to obtain **3aq** (white solid, 73.4 mg, 80% yield). M. p.: 191-193 ˚C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.57 (d, J = 7.2 Hz, 4H), 7.50 (dd, J = 7.6, 1.2 Hz, 2H), 7.48-7.30 (m, 10H), 7.28-7.18 (m, 6H), 6.67 (d, J = 8.4 Hz, 4H); ^{13}C NMR

(100 MHz, $CDCl_3$): δ 140.9, 140.5, 140.0, 139.9, 138.6, 131.7, 129.8, 129.5, 128.7, 127.6, 127.3, 127.1, 126.9, 126.1; MS (EI): m/z (%) 458 (M^+, 100).

2,2'-di(furan-2-yl)-1,1'-biphenyl (3ar). The crude product was purified by flash chromatography (hexane) to obtain **3ar** (white solid, 15.5 mg, 27% yield). M. p.: 148-153 ℃. ^1H NMR (400 MHz, $CDCl_3$): δ 7.92 (d, J = 8.0 Hz, 2H), 7.48-7.42 (m, 2H), 7.34-7.26 (m, 4H), 7.18 (d, J = 7.6 Hz, 2H), 6.12 (q, J = 1.6 Hz, 2H), 5.36 (d, J = 3.6 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 152.1, 141.3, 138.2, 130.4, 129.6, 127.9, 127.4, 126.1, 111.4, 108.5; HRMS (EI) for $C_{20}H_{14}O_2$: calculated $[M]^+$, 286.0994. Found, 286.0993.

2,2'-di(thiophen-3-yl)-1,1'-biphenyl (3as). The crude product was purified by flash chromatography (hexane) to obtain **3as** (white solid, 28.7 mg, 45% yield). M. p.: 111-113 ℃. ^1H NMR (400 MHz, $CDCl_3$): δ 7.40-7.28 (m, 8H), 6.96 (dd, J = 5.2, 3.2 Hz, 2H), 6.51 (dd, J = 2.8, 1.2 Hz, 2H), 6.44 (dd, J = 4.8, 1.2 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 141.5, 140.0, 135.8, 131.1, 129.3, 128.2, 127.6, 127.1, 123.7, 122.3; HRMS (EI) for $C_{20}H_{14}S_2$: calculated $[M]^+$, 318.0537. Found, 318.0541.

General Procedure for the Synthesis of 3ba–3ja

Phenyl boronic acid **2a** (53.6 mg, 0.44 mmol, 2.2 eq.), $Pd(dba)_2$ (1.15 mg, 0.002 mmol, 1 mol %) were added to a reaction tube. Then 2 mL DCM was added using a syringe. The reaction mixture was stirred 15 min, then cyclic dibenziodoniums **1** (0.2 mmol, 1.0 eq.) and K_3PO_4 (212.3 mg, 1.0 mmol, 5.0 eq.) in 2.4 mL DCM were added. The reaction was stirred at room temperature for 12 hours. After the solvent was removed in *vacuo* and the residue was purified by silica gel using eluent (hexane) to afford the desired products except **3ba-3ja** (using a proper mixture of eluents of

hexane/ ethyl acetate).

3',5'-Dimethyl-1,1':2',1'':2'',1'''-quaterphenyl (3ba). The crude product was purified by flash chromatography (hexane) to obtain **3ba** (white solid, 56.2 mg, 84% yield). M. p.: 97-99 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.29 (d, J = 2.8 Hz, 3H), 7.23-7.17 (m, 1H), 7.14-7.01 (m, 5H), 6.98 (t, J = 6.8 Hz, 2H), 6.85 (s, 1H), 6.67-6.58 (m, 4H), 2.34 (s, 3H), 2.17 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 141.59, 141.28, 141.14, 141.05, 138.2, 136.63, 136.57, 136.49, 132.3, 130.0, 129.8, 129.6, 128.9, 128.4, 127.3, 127.2, 127.0, 126.5, 126.1, 125.7, 21.3, 21.1; HRMS (EI) for $C_{26}H_{22}$: calculated $[M]^+$, 334.1722. Found, 334.1721.

4''-Chloro-1,1':2',1'':2'',1'''-quaterphenyl (3ca). The crude product was purified by flash chromatography (hexane) to obtain **3ca** (white solid, 47.7 mg, 70% yield). M. p.: 115-119°C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.39-7.29 (m, 5H), 7.19-7.13 (m, 2H), 7.13-7.06 (m, 2H), 7.01 (q, J = 7.6 Hz, 4H), 6.62-6.55 (m, 4H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 142.6, 141.0, 140.6, 139.6, 138.7, 138.5, 133.1, 132.9, 131.5, 130.0, 129.8, 129.1, 129.0, 127.7, 127.6, 127.1, 127.0, 126.4, 126.1; HRMS (EI) for $C_{24}H_{17}Cl$: calculated $[M]^+$, 340.1019. Found, 340.1016.

4''-Bromo-1,1':2',1'':2'',1'''-quaterphenyl (3da). The crude product was purified by flash chromatography (hexane) to obtain **3da** (white solid, 66.3 mg, 86% yield). M. p.: 109-113 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.47 (dd, J = 8.0, 2.0 Hz, 1H), 7.38-7.30 (m, 4H), 7.28 (d, J = 8.4 Hz, 1H), 7.20-7.13 (m, 1H), 7.13-7.06 (m, 2H), 7.06-6.96 (m, 4H), 6.59 (td, J = 8.4, 0.8 Hz, 4H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 142.9, 140.9, 140.6, 139.5, 139.0, 138.7, 133.1, 132.7, 131.5, 130.1, 130.0, 129.1, 129.0, 127.8, 127.58,

127.56, 127.2, 126.5, 126.1, 121.3; HRMS (EI) for $C_{24}H_{17}Br$: calculated $[M]^+$, 384.0514. Found, 384.0506.

4''-Methoxy-1,1':2',1'':2'',1'''-quaterphenyl (3ea). The crude product was purified by flash chromatography (hexane/ethyl acetate = 200:1) to obtain **3ea** (white solid, 59.2 mg, 88% yield). M. p.: 113-119 °C. ^{1}H NMR (400 MHz, $CDCl_3$) *δ*: 7.40-7.36 (m, 1H), 7.36-7.27 (m, 3H), 7.18-7.13 (m, 1H), 7.12-7.05 (m, 2H), 7.01 (q, *J* = 6.8 Hz, 4H), 6.91 (dd, *J* = 8.4, 2.4 Hz, 1H), 6.73 (s, 1H), 6.66-6.60 (m, 4H), 3.83 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) *δ*: 158.8, 142.1, 141.1, 140.9, 139.6, 132.7, 132.6, 131.8, 129.9, 129.2, 129.1, 127.4, 127.2, 127.0, 126.0, 125.8, 115.2, 112.6, 55.3; HRMS (EI) for $C_{25}H_{20}O$: calculated $[M]^+$, 336.1514. Found, 336.1508.

4''-Phenyl-1,1':2',1'':2'',1'''-quaterphenyl (3fa). The crude product was purified by flash chromatography (hexane) to obtain **3fa** (white solid, 66.6 mg, 87% yield). M. p.: 111-114 °C. ^{1}H NMR (400 MHz, $CDCl_3$): *δ* 7.70-7.64 (m, 2H), 7.62 (dd, *J* = 8.0, 2.0 Hz, 1H), 7.52-7.41 (m, 5H), 7.41-7.31 (m, 3H), 7.23-7.17 (m, 1H), 7.15-7.06 (m, 2H), 7.06-6.97 (m, 4H), 6.72-6.63 (m, 4H); ^{13}C NMR (100 MHz, $CDCl_3$): *δ* 141.4, 141.0, 140.9, 140.6, 140.1, 139.6, 139.1, 132.2, 131.7, 130.0, 129.2, 128.8, 128.7, 127.5, 127.3, 127.1, 127.0, 126.0, 125.9, 125.6; HRMS (EI) for $C_{30}H_{22}$: calculated $[M]^+$, 382.1722. Found, 382.1718.

2-([1,1'-Biphenyl]-2-yl)-1-phenylnaphthalene (3ga). The crude product was purified by flash chromatography (hexane) to obtain **3ga** (white solid, 27.8 mg, 39% yield). M. p.: 122-127 °C. ^{1}H NMR (400 MHz, $CDCl_3$): *δ* 7.87 (d, *J* = 8.0 Hz, 1H), 7.81 (d, *J* = 8.4 Hz, 1H), 7.53 (d, *J* = 8.8 Hz, 1H), 7.50-7.41 (m, 2H), 7.36-7.20 (m, 5H), 7.20-7.14 (m, 2H), 7.13-6.99 (m, 5H), 6.91 (dd, *J* = 8.0, 1.6 Hz, 2H), 6.47 (d, *J* = 7.2 Hz, 1H); ^{13}C

NMR (100 MHz, $CDCl_3$): δ 141.1, 140.8, 140.1, 138.3, 137.9, 137.8, 132.7, 132.5, 132.1, 131.3, 131.0, 129.9, 129.7, 129.5, 127.8, 127.6, 127.4, 127.22, 127.20, 127.0, 126.6, 126.4, 126.3, 126.2, 125.9, 125.5; HRMS (EI) for $C_{28}H_{20}$: calculated $[M]^+$, 356.1565. Found, 356.1559.

4''-Methyl-1,1':2',1'':2'',1'''-quaterphenyl (3ha). The crude product was purified by flash chromatography (hexane) to obtain **3ha** (white solid, 46.7 mg, 73% yield). M. p.: 103-107 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.41-7.36 (m, 1H), 7.36-7.27 (m, 3H), 7.19-7.13 (m, 2H), 7.08 (q, J = 7.2 Hz, 2H), 7.04-6.95 (m, 5H), 6.62 (t, J = 7.2 Hz, 4H), 2.38 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 141.06, 141.01, 140.8, 139.2, 137.05, 136.97, 131.8, 131.5, 130.7, 129.9, 129.20, 129.17, 127.8, 127.39, 127.35, 127.2, 127.0, 125.8, 21.1; HRMS (EI) for $C_{25}H_{20}$: calculated $[M]^+$, 320.1565. Found, 320.1569.

4'',5'-Dichloro-1,1':2',1'':2'',1'''-quaterphenyl (3ia). The crude product was purified by flash chromatography (hexane) to obtain **3ia** (white solid, 47.3 mg, 63% yield). M. p.: 147-152 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.35-7.26 (m, 4H), 7.16 (d, J = 2.0 Hz, 2H), 7.12 (t, J = 7.2 Hz, 2H), 7.03 (t, J = 7.6 Hz, 4H), 6.60-6.53 (m, 4H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 142.6, 139.4, 137.3, 133.5, 132.8, 130.0, 128.9, 127.7, 127.2, 126.6; HRMS (EI) for $C_{24}H_{16}Cl_2$: calculated $[M]^+$, 374.0629. Found, 374.0634.

4''-(Trifluoromethyl)-1,1':2',1'':2'',1'''-quaterphenyl (3ja). The crude product was purified by flash chromatography (hexane) to obtain **3ja** (white solid, 45.7 mg, 61% yield). M. p.: 107-112 °C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.60-7.49 (m, 2H), 7.40 (s, 1H), 7.40-7.33 (m, 3H), 7.19-7.14 (m, 1H), 7.10 (q, J = 7.2 Hz, 2H), 7.01 (td, J = 7.6, 3.6 Hz, 4H), 6.57 (t, J = 8.0 Hz, 4H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 143.9, 141.8, 141.1, 140.6,

139.7, 138.8, 132.2, 131.6, 130.3, 130.0, 129.3, 129.2, 128.2, 127.81, 127.78, 127.4, 127.0 (q, J = 3.1 Hz), 126.8, 126.4, 124.4 (q, J = 271.0 Hz), 123.8 (q, J = 3.5 Hz); HRMS (EI) for $C_{25}H_{17}F_3$: calculated $[M]^+$, 374.1282. Found, 374.1276.

General Procedure for the Synthesis of 4.

ortho-Tetraaryl **3aj** (66.9 mg, 0.2 mmol, 1.0 eq.), 20 mL DCM (distilled) were added to a Schlenk tube. Then 1 mL CF_3SO_3H and DDQ (90.8 mg, 0.4 mmol, 2.0 eq.) were subsequently added using a syringe at ~0 ˚C. The reaction was stirred at 0˚C for 3 hours. After completion of the reaction, it was quenched with a saturated aqueous solution of $NaHCO_3$ (20 mL). The dichloromethane layer was separated and washed with water and brine solution, then dried over anhydrous Na_2SO_4 and filtered. The solvent was removed in *vacuo* and the residue was purified by silica gel using a proper eluent (hexane) to afford the desired product **4** (white solid, 36.6 mg, 55% yield). M. p.: 165-171 ˚C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.82 (s, 1H), 8.72-8.58 (m, 3H), 8.55 (d, J = 8.0 Hz, 1H), 8.51 (s, 1H), 7.87 (d, J = 8.4 Hz, 1H), 7.72 (d, J = 8.0 Hz, 2H), 7.67-7.60 (m, 2H), 7.50 (d, J = 8.4 Hz, 1H), 7.36 (d, J = 7.6 Hz, 2H), 2.63 (s, 3H), 2,46 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 139.7, 138.4, 137.3, 136.9, 129.9, 129.82, 129.79, 129.6, 129.3, 128.79, 128.76, 127.7, 127.3, 127.1, 126.8, 126.1, 123.8, 123.29, 123.25, 123.1, 121.4, 21.9, 21.2; HRMS (EI) for $C_{26}H_{20}$: calculated $[M]^+$, 332.1565. Found, 332.1562.

General Procedure for the Synthesis of 7.[22]

2,2'-Biphenyldiboronic acid **6** (26.6 mg, 0.11 mmol, 1.1 eq.), $Pd(dba)_2$ (5.75 mg, 0.01 mmol, 10 mol %), cyclic dibenziodoniums **1a** (42.8 mg, 0.1 mmol, 1.0 eq.), K_3PO_4 (106.1 mg, 0.5 mmol, 5.0 eq) in 4 mL DCM were added to a Schlenk tube under

argon. The reaction was stirred at room temperature for 12 hours. After the solvent was removed in *vacuo* and the residue was purified by silica gel using eluent (hexane) to afford the desired products **7** (white solid, 6.4 mg, 21% yield). M. p.: 233-237 ˚C. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.31-7.26 (m, 8H), 7.20-7.12 (m, 8H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 141.5, 129.0, 127.2; MS (EI): m/z (%) 304 (M^+, 100).

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Supporting Information

The copies of ^{1}H, ^{13}C NMR spectra for all products. The Supporting Information is available free of charge via the internet at http://pubs.acs.org.

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