2,3,10,11-Tetrahydroxytetraphenylene and Its Application in Molecular Recognition

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Dedicated to Professor *Dieter Seebach* on the occasion of his 75th birthday

A rationally designed 2,3,10,11-tetrahydroxytetraphenylene (**1**) has been synthesized. Employing **1** as a building block, a structurally novel tweezer-like host **2** containing dibenzo-24-crown-8 moieties has been prepared. Host **2** showed excellent molecular-recognition ability toward paraquat (=1,1′-dimethyl-4,4′-bipyridinium dichloride) derivative **3a** to form a 1:1 stable complex in solution.

Introduction. – The design and synthesis of novel host molecules that are able to form stable complexes with guest molecules in stable and selective manner is a challenging topic in the development of supramolecular chemistry [1]. Over the past decades, various synthetic hosts (such as crown ethers, cryptands, cyclodextrins, calixarenes, cavitands, cyclophanes, cucurbiturils, calixpyrroles, cyclopeptides, *etc.*) have been developed, and they all played important roles in the field of host–guest chemistry [1][2]. As can be seen, these classical hosts all contain building blocks with specific geometries and reactivities. To develop new hosts with unique structures and properties, the design and synthesis of novel building blocks is, therefore, an important prerequisite.

Tetraphenylene (=tetrabenzocyclooctatriene) [3] is a structurally interesting saddle-shaped molecule, in which four benzene rings are *ortho*-linked to form an eight-membered ring. Furthermore, all benzene rings are oriented above and below the average molecular plane [4][5]. The first reliable synthesis of tetraphenylene was reported in 1943 [3]. Since then, there have been a vast amount of studies on the chemistry and physics of this geometrically unique compound as well as its analogs [5]. However, at the early stage of development, synthetic chemists, for most of the time, only focused on the synthesis of tetraphenylene itself and its derivatives [6–13]. Until the beginning of the 21st century, potential applications of tetraphenylene derivatives

[1]) An Area of Excellence Scheme established under the University Grants Committee (Hong Kong).

have gradually been explored. In recent years, more frequent applications in molecular devices [14], materials science [15][16], supramolecular chemistry [17][18], and asymmetric catalysts [17b][19] have received considerable attention.

Although tetraphenylene and its derivatives have attracted increasing interests in many research areas, the host–guest chemistry based on tetraphenylene-derived hosts [18] has been scarcely explored. We envisaged that polyhydroxytetraphenylenes [16][17][19][20], a class of interesting compounds not only with unique three-dimensional rigid structure but also with rich reactive sites, could be utilized as promising building blocks for the construction of novel hosts through functionalizations of their OH groups by covalent bonds or metal ions. In this way, further development of new supramolecular systems with specific structures and properties can be accomplished.

Recently, design and synthesis of molecular tweezers have become a very active research area due to their intriguing structures and potential applications in supramolecular chemistry [21]. An intriguing example was recorded in 2007. *Sygula et al.* reported an interesting tetraphenylene-based molecular tweezer **A** with two corannulene subunits that can be positioned to embrace a molecule of C_{60}, forming a 1:1 inclusion complex through 'pure' concave–convex π–π interactions [18]. Moreover, *Chen* and co-workers utilized triptycene as a building block to synthesize tweezer-like hosts **B** and **C**, which could form stable complexes with paraquat (=1,1′-dimethyl-4,4′-bipyridinium dichloride) derivatives [22][23] (*Fig. 1*). Inspired by these elegant works, we considered that, if four OH groups are placed in positions 2, 3, 10, and 11 of tetraphenylene, the resulting 2,3,10,11-tetrahydroxytetraphenylene (**1**) would become an excellent building block for the construction of novel molecular tweezers.

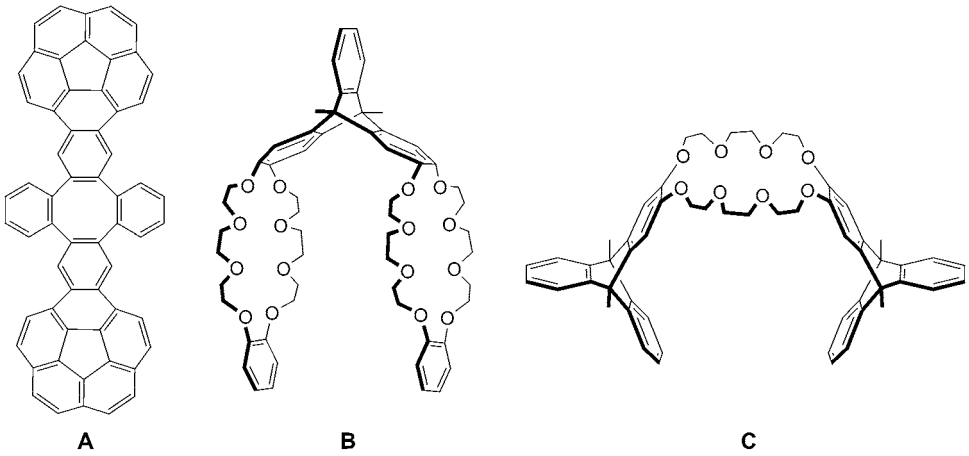


Fig. 1. *Structures of some molecular tweezers*

In this article, we would like to disclose the synthesis of 2,3,10,11-tetrahydroxytetraphenylene (**1**) and a novel tetraphenylene-based tweezer-like host **2** containing two dibenzo-24-crown-8 moieties, in which two electron-rich lateral cavities and one clip-like central cavity are featured. Furthermore, the binding properties of **2** have also been studied. Owing to the electron-rich cavities, host **2** showed excellent molecular

recognition ability towards paraquat derivative **3a** to form a 1:1 stable complex in solution (*Fig. 2*).

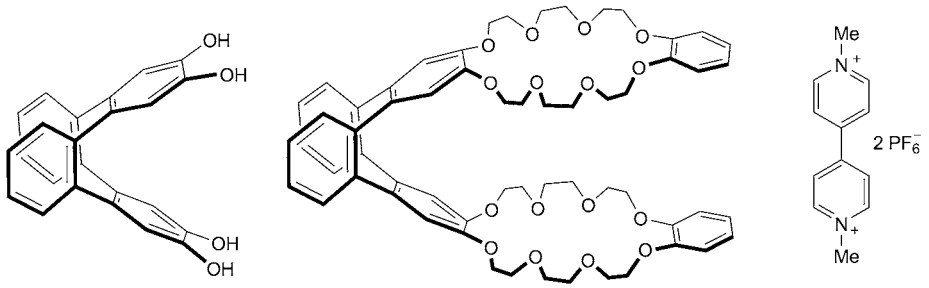


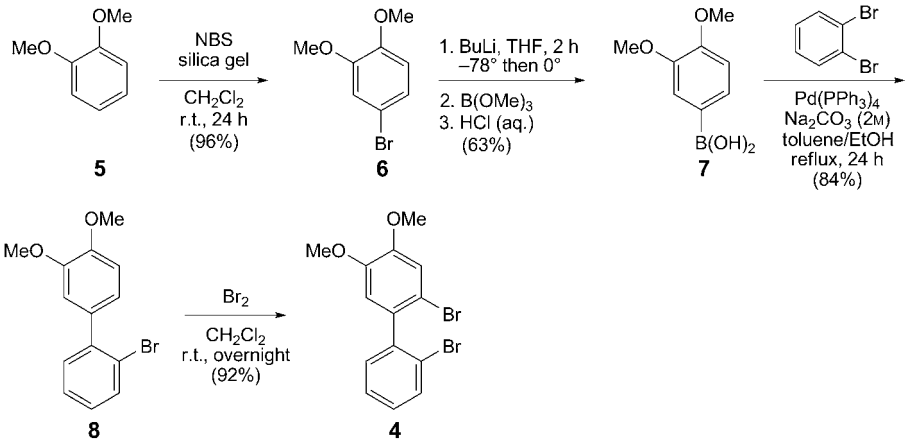
Fig. 2. *Structures of building block* **1**, *molecular tweezers host* **2**, *and paraquat derivative* **3a**

Results and Discussion. – There are four approaches towards the construction of tetraphenylene frameworks: *a*) homo-coupling of 2,2′-dimetal-1,1′-biphenyl [6–9], *b*) metal-mediated high-temperature pyrolysis of biphenylene [10], *c*) *Diels–Alder* cycloaddition between 1,2,5,6-dibenzocycloocta-3,7-diyne and furan with subsequent deoxygenation [11], and *d*) cationic Rh-catalyzed double [2+2+2] cycloaddition of triyne [12]. An assessment of the synthetic works concerning tetraphenylene derivatives in our laboratories [17][20] and those reported by the others [6–12] has led us to decide that Cu^{II}-mediated oxidative coupling reactions of 2,2′-dihalo-4,5-dimethoxy-1,1′-biphenyl should provide a straightforward and concise approach to 2,3,10,11-tetrahydroxytetraphenylene (**1**). The key starting material 2,2′-dibromo-4,5-dimethoxybiphenyl (**4**) was synthesized as illustrated in *Scheme 1*. Thus, bromination of 1,2-dimethoxybenzene (**5**) with *N*-bromosuccinimide (NBS) catalyzed by silica gel (100–200 mesh) selectively gave 4-bromo-1,2-dimethoxybenzene (**6**) in excellent yield of 96% [24]. Treatment of **6** with BuLi, followed by $B(OMe)_3$ with subsequent quenching by aq. HCl, afforded the corresponding (3,4-dimethoxyphenyl)boronic acid (**7**) in 63% yield [25]. Next, a *Suzuki* coupling reaction between **7** and 1,2-dibromobenzene was conducted to afford the 2-bromo-3′,4′-dimethoxybiphenyl (**8**) in 84% yield [26]. Another bromination reaction of **8** with Br_2 completed the synthesis of 2,2′-dibromo-4,5-dimethoxybiphenyl (**4**) in 92% yield [26].

With compound **4** in hand, the construction of 2,3,10,11-tetrahydroxytetraphenylene (**1**) was then carried out. Treatment of **4** with BuLi [20d] generated a double Li/Br-exchanged intermediate **9**, to which anhydrous $CuCl_2$ was added. The corresponding oxidative coupling product **10** together with its isomer **11** were obtained as a mixture in 34% yield by column chromatography employing hexane/CH_2Cl_2 4:1 as an eluent. The ratio **10**/**11** was determined as *ca.* 1:2 by ^{1}H-NMR spectroscopic analysis on a mixture **10**/**11** in CD_3CN (*Scheme 2*).

To obtain pure 2,3,10,11-tetramethoxytetraphenylene (**10**) as the precursor of **1**, purification was achieved by careful oft-repeated column chromatography separation with hexane/CH_2Cl_2/AcOEt 15:10:1 as an eluent. The structures of **10** and **11** were confirmed by ^{1}H- and ^{13}C-NMR spectroscopy, and HR-mass spectrometry, respectively.

Scheme 1



The structure of **10** was further confirmed by an X-ray crystallographic study (*Fig. 3*). Finally, demethylation of **10** with BBr_3 afforded the desired 2,3,10,11-tetrahydroxytetraphenylene (**1**) in excellent yield of 98% (*Scheme 2*, *Route A*).

In addition, due to the inefficiency of purification step of **10** and **11** with oft-repeated column chromatography, an alternative and efficient method for the isolation was desired. Fortunately, after demethylation of these two isomers by using BBr_3, and without further separation and purification, we uncovered that an excellent separation

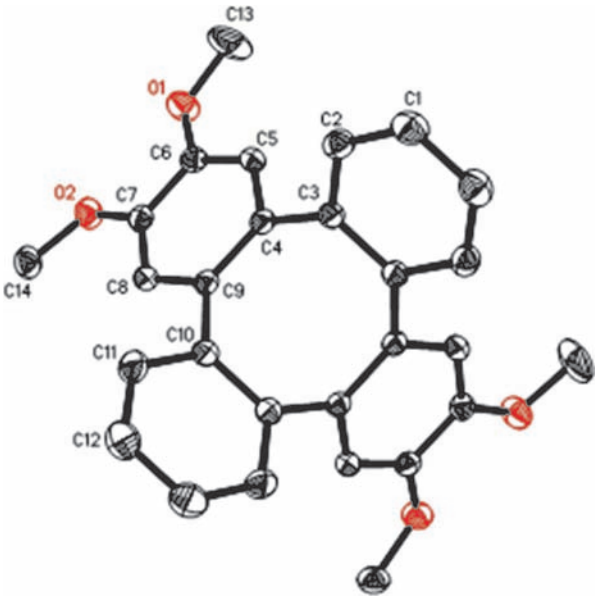
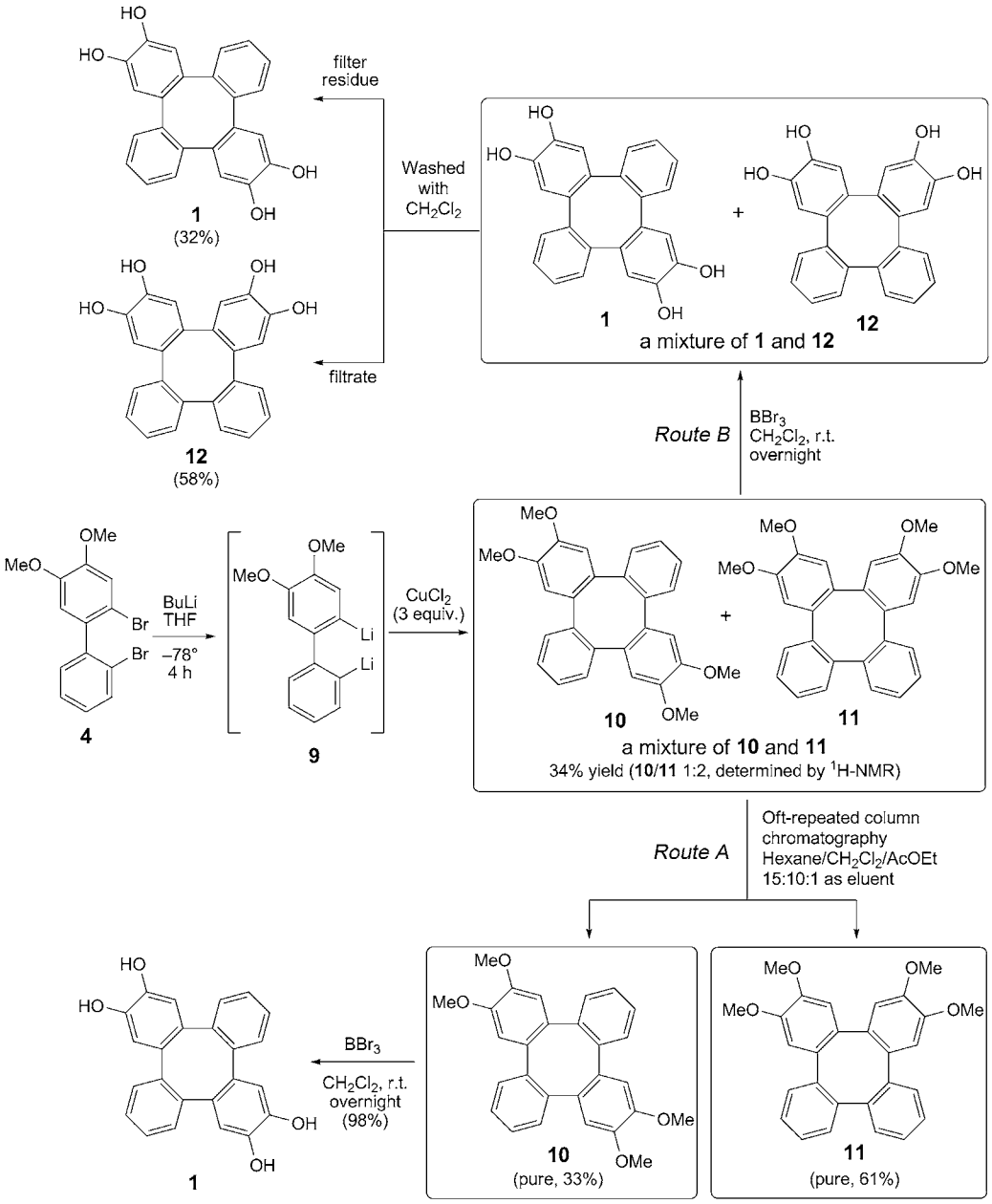


Fig. 3. *ORTEP Drawing of* **10**. H-Atoms have been omitted for clarity.

Scheme 2

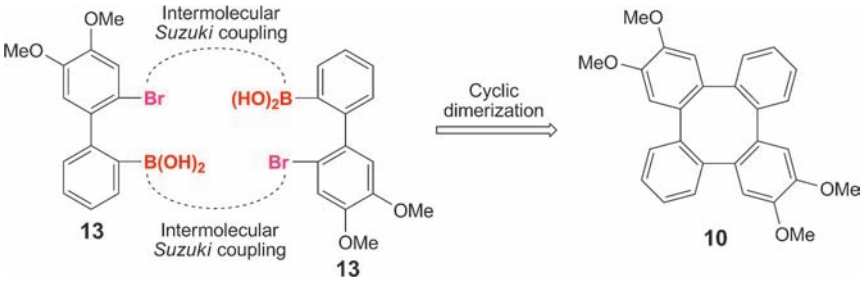


was achieved by simply washing the resulting mixture of **1** and **12** with CH_2Cl_2. Compound **1** was collected from the filtering residue, while the filtrate was dried under vacuum to provide **12**. Both analytically pure samples **1** and **12** were easily obtained by

flash column chromatography. In comparison with the direct chromatographic separation of mixture **10**/**11**, the latter procedure was found to be much more convenient to accumulate the pivotal compound **1** (*Scheme 2*, *Route B*).

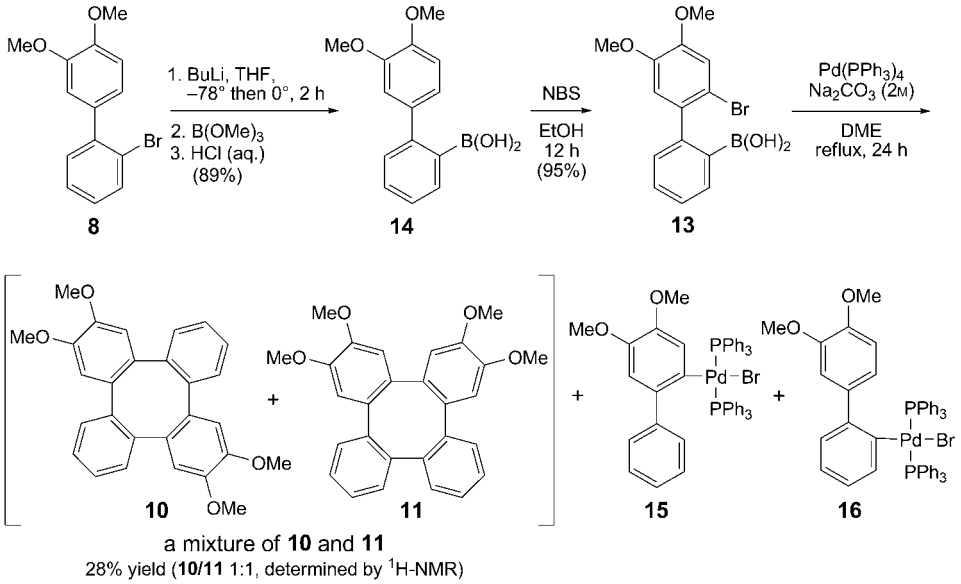
Another reliable way in which **1** can be synthesized is *Suzuki* coupling [27]. As such, synthon **13** was designed for an intermolecular *Suzuki* coupling reaction, as depicted in *Scheme 3*. We hypothesized that the *inter*molecular cyclic dimerization of Br and $B(OH)_2$ groups of compound **13** would lead to a straightforward regio- and stereoselective synthesis of 2,3,10,11-tetramethoxytetraphenylene (**10**).

Scheme 3



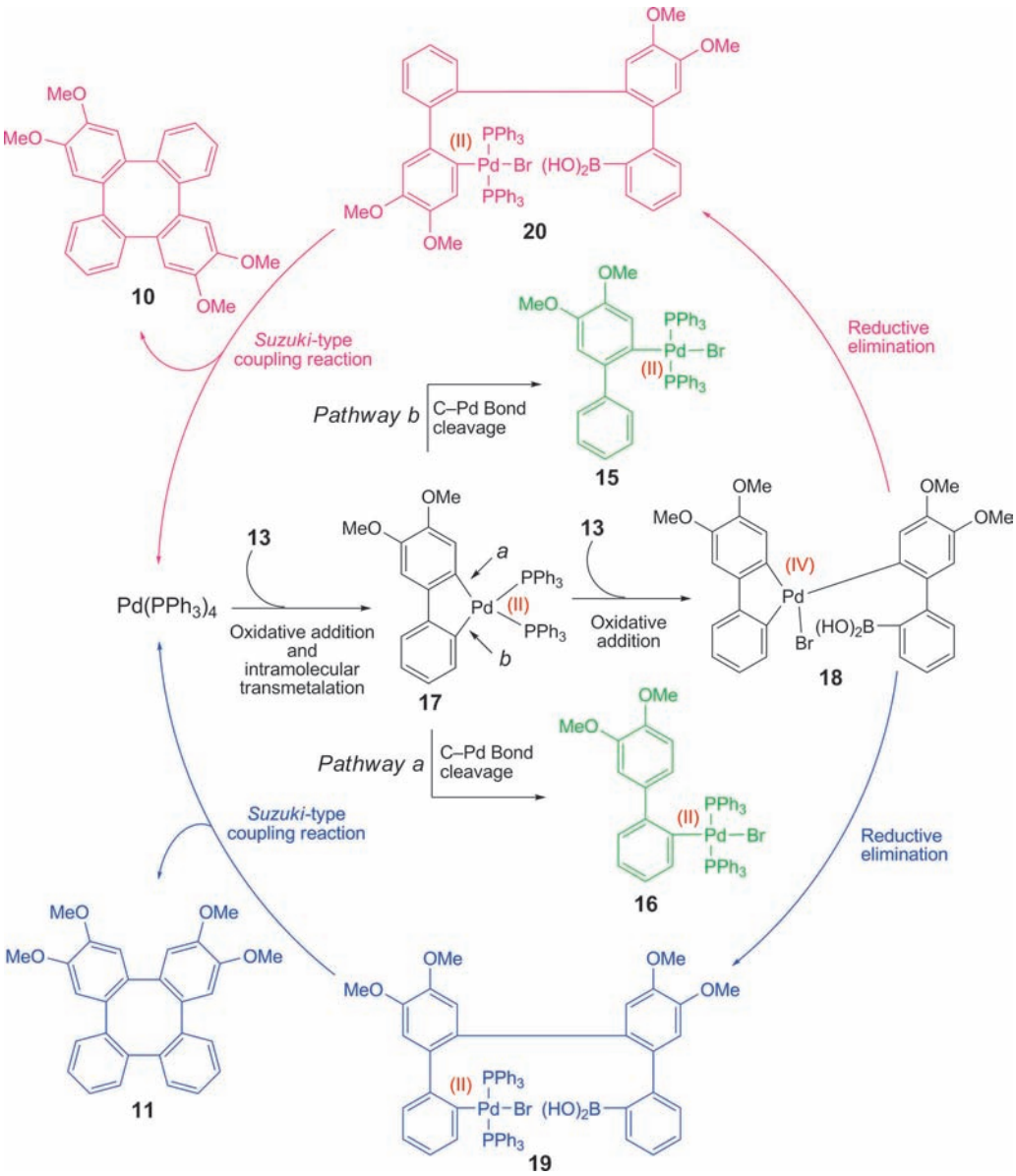
With this in mind, we first investigated the synthesis of compound **13** starting from biphenyl **8** (*Scheme 4*). Treatment of **8** with BuLi, followed by addition of $B(OMe)_3$ and quenching the reaction with aq. HCl, afforded the corresponding boronic acid **14** [25]. Subsequent bromination of the boronic acid **14** with NBS gave **13** [24].

Scheme 4



Subsequently, compound **13** was allowed to undergo *Suzuki* coupling reaction [27]. However, the result was unexpected because a mixture of **10** and **11** in equal quantities was obtained, as confirmed by ^{1}H-NMR spectroscopic analysis. The generation of **11** was intriguing, and a plausible catalytic cycle is proposed [28] (*Scheme 5*). As can be seen, Pd^0 species undergos a tandem oxidative addition to the relatively weak aryl–Br

Scheme 5



bond. Then, an intramolecular cyclometalation affords palladacycle **17**. Subsequently, **17** might undergo a second oxidative addition with another molecule of **13** to form the Pd^{IV} intermediate **18**. A reductive elimination of **18** may afford intermediates **19** and **20** in a competitive manner. A second intramolecular *Suzuki*-type coupling reaction of **19** or **20** will lead to the formation of tetraphenylenes **10** or **11**, respectively. In addition, the C–Pd bond cleavage of palladacycle **17** affords isolable intermediates **15** and **16** (*Fig. 4*), providing a strong evidence for the formation of palladacycle **17**. This result can also explain the dramatically low yield of **10** and **11** under *Suzuki* coupling reaction conditions due to the interrupted catalytic recycle by this C–Pd bond cleavage. However, various mechanisms of Pd-catalyzed coupling reactions of aryl halides and boronic acids have previously been proposed [27b][29], other pathways leading to compound **11** cannot be ruled out because of our own failure to capture the palladacycle intermediate.

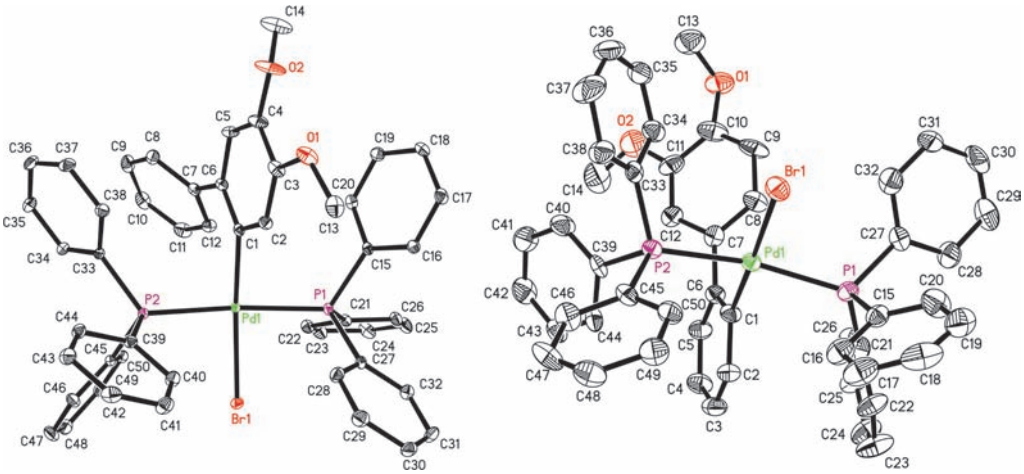
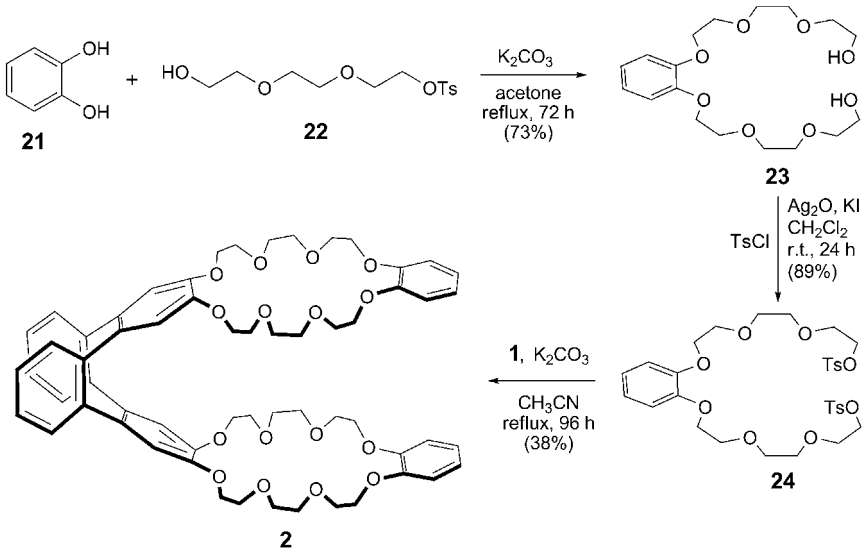


Fig. 4. *ORTEP Drawings of* **15** (left) *and* **16** (right). H-Atoms have been omitted for clarity.

With tetrahydroxytetraphenylene **1** in hand, we next sought to prepare tetraphenylene-based tweezer-like host molecule **2**. The synthetic procedure was outlined in *Scheme 6*. First, 1,2-bis(2-{2-[(2-tosyloxy)ethoxy]ethoxy}ethoxy)benzene **24** was obtained by a nucleophilic substitution of catechol (**21**) with 8-tosyloxy-3,6-dioxaoctanol (**22**) in the presence of K_2CO_3 [22b][30] (→**23**), followed by reaction with TsCl in the presence of silver oxide [30]. Then, **1** was allowed to react with 2 equiv. of **24** in MeCN in the presence of K_2CO_3 under a high-dilution condition to afford **2** in 38% yield [22b]. The structure of **2** shows that the tetraphenylene unit is linked with two benzo-24-crown-8 units to form two dibenzo-24-crown-8 lateral cavities and one clip-like central cavity, which are electron-rich for inclusion of some electron-deficient guests. Host **2** was characterized by ^{1}H- and ^{13}C-NMR spectroscopy, as well as by MALDI-TOF-MS and element analyses.

Scheme 6



Host–guest studies of **2** with electron-deficient paraquat derivatives **3** were carried out in $CDCl_3/CD_3CN$ 1:1 [22b][30]. When host **2** (in $CDCl_3/CD_3CN$ 1:1, 10 mM) and paraquat derivative **3a** (in $CDCl_3/CD_3CN$ 1:1, 10 mM) were mixed, the solution showed a distinct and swift color change from colorless to bright orange-yellow due to charge transfer between the electron-rich aromatic rings of the host **2** and the electron-poor pyridinium rings of the guest **3a** [22][30]. Moreover, when the solvent was evaporated, the resulting solid showed an orange color, although both host **2** and guest **3a** are white solids. As shown in *Fig. 5*, the ^{1}H-NMR spectrum of a 1:1 mixture **2**/**3a** in $CDCl_3/CD_3CN$ (1:1) showed a distinct difference from those of host **2** and guest **3a**. The proton H_6 of the paraquat ring showed a significant upfield shift (0.841 ppm), which may be due to the strong shielding effect of the aromatic rings of **2** [22]. Similarly, all H_1–H_5 signals of **2** showed upfield shifts. Protons H_4 and H_5 did not only exhibit significant upfield shifts of 0.245 and 0.455 ppm, respectively, but also changed obviously from one set of resonances to two sets of resonances. In contrast, considerable downfield shifts of the Me H-atoms (0.243 ppm) as well as H_7 (0.262 ppm) of guest **3a** was observed, which were attributed to their positions in the deshielding region of the aromatic rings of **2** [22]. These observations jointly indicated that a stable complex between **2** and guest **3a** was formed.

Furthermore, UV spectroscopic titrations [31] afforded a quantitative estimate for the complex of **2** and **3a** by monitoring the changes of absorbance at 221 nm. The results showed that a 1:1 complex **2**·**3a** was formed (*Job*'s plot; *Fig. 6*,*a*). The electrospray ionization mass spectrum (ESI-MS) provided further evidence for the formation of complex **2**·**3a** (*Fig. 6*,*b*). As a result, the strongest peak at *m*/*z* 615.3 for [**2**·**3a**-2PF_6^-]$^{2+}$ was obviously observed, indicating that the 1:1 stable complex between host **2** and guest **3a** was formed. The apparent association constant between **2** and

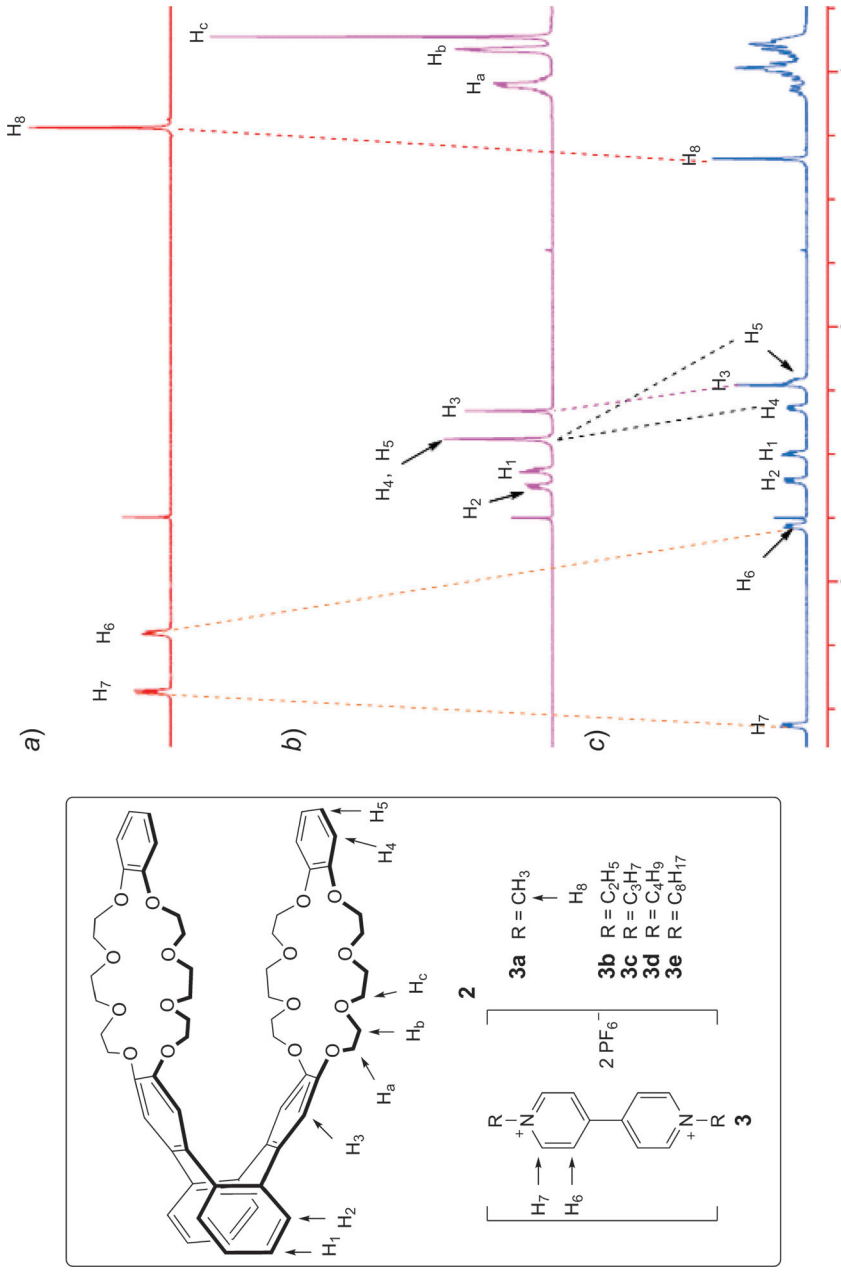


Fig. 5. *The H-atom assignments of the host* **2** *and guest* **3a**, *as well as partial* ^{1}*H-NMR spectra* (300 MHz, $CDCl_3/CD_3CN$ 1 : 1, 298 K) *of* a) *free guest* **3a**, b) *free host* **2**, *and* c) **2** *and 1.0 equiv. of* **3a**. $[\mathbf{2}]_0 = 10$ mM.

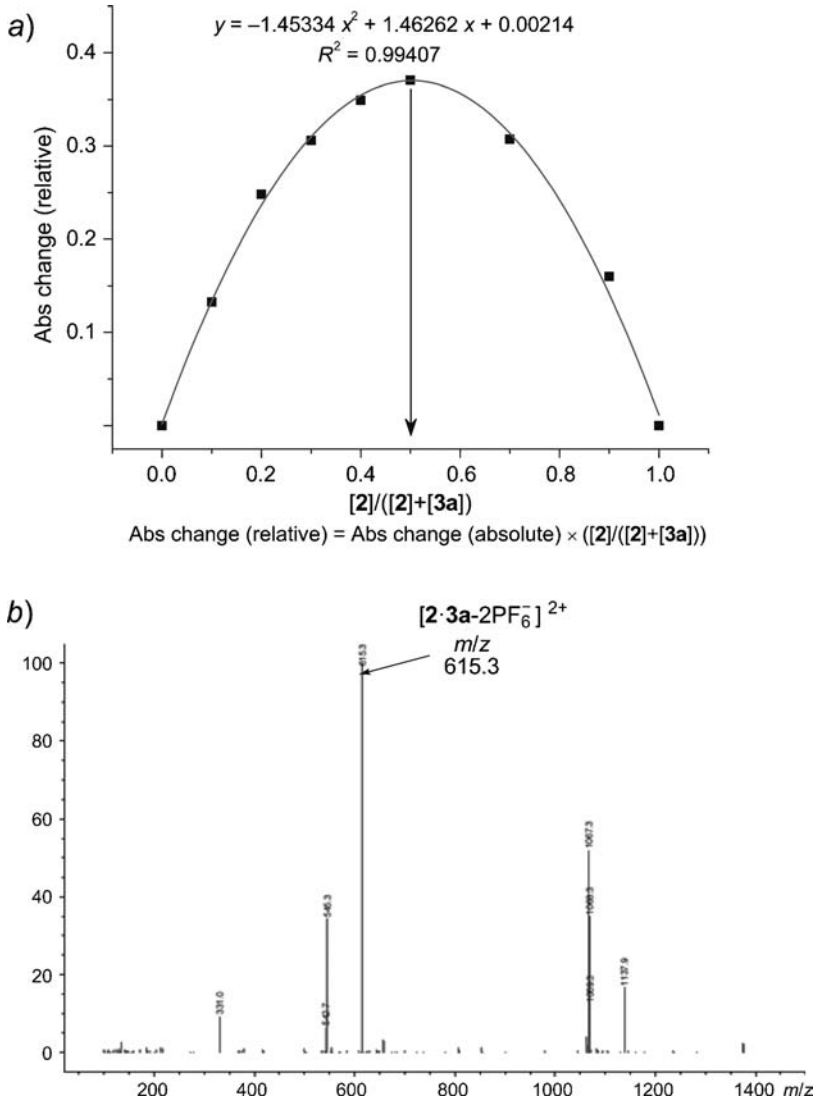


Fig. 6. a) Job's *plot: absorbance change at 220 nm of* **2** vs. *[**2**]/([**2**] + [**3a**]) in MeCN at 25°* (the overall concentration 2.0×10^{-5} M). b) *ESI-MS of the complex* **2** · **3a**.

paraquat **3a** was calculated by a competitive method as $K_{a,exp,\mathbf{2}\cdot\mathbf{3a}} = 4.59(\pm 0.24) \times 10^3\ M^{-1}$ [22][30][32].

Moreover, complexation of host **2** with paraquat derivatives **3b**–**3e** was also investigated (*Fig. 5*). However, only slight color changes of the mixed solutions of **2** and **3b**–**3e** were observed. A series of ^{1}H-NMR experiments of the complexes were conducted; compared to the free host **2**, no significant proton shifts of the complexes

were observed in the spectra, suggesting weak recognition abilities of host **2** toward guests **3b**–**3e**.

Conclusions. – In summary, we disclosed herein the synthetic approach towards a rationally designed 2,3,10,11-tetrahydroxytetraphenylene (**1**), which was used as a building block to construct the novel tweezer-like host **2**. Excellent molecular-recognition ability toward paraquat derivative **3a** was demonstrated by **2**, forming a 1:1 stable complex with **3a** in solution. Design and synthesis of other molecular tweezers with novel structural motifs based on tetraphenylenes are now in progress.

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Experimental Part

General. Commercially available materials were used without further purification. For reactions requiring anh. conditions, solvents and reagents were dried and purified by the usual techniques. Reactions were monitored by TLC (detection with UV light). Flash chromatography (FC): silica gel (300–400 mesh). M.p.: *Shanghai Shenguang SGW XT-4* instrument (uncorrected). UV Titrations: *Varain Cary100* UV/VIS spectrophotometer. IR Spectra: *FT-IR Bio-Rad FTS-185* spectrometer; $\tilde{\nu}_{max}$ in cm^{-1}. ^{1}H-NMR Spectra: *Bruker AM300* (300 MHz), *Varian Mercury 300* (300 MHz), and *Varian Mercury 400* (400 MHz) NMR spectrometers. ^{31}P-NMR Spectra: *Varian Mercury 300* (121 MHz) NMR spectrometer. ^{13}C-NMR Spectra: *Bruker DPX-400* (100 MHz), *Varian Mercury 300* (75 MHz), and *Varian Mercury 400* (100 MHz) spectrometers. Chemical shifts δ in ppm from Me_4Si on the scale with the solvent resonance employed as the internal standard; *J* in Hz. MS: *HP HP5989A*, *Agilent HP5873*, *Waters GCT premier*, *Agilent LC-MS 6120*, *Agilent 1100-MSD*, *Bruker Daltonics FTMS-7*, *IonSpec 4.7T*, and *Varian 4.7T MALDI-FTMS* spectrometers; *m*/*z* (rel. int.). Elemental analyses: *Elemantar Vario EL* spectrometer.

4-Bromo-1,2-dimethoxybenzene (**6**). To a soln. of 1,2-dimethoxybenzene (27.6 g, 200 mmol) in CH_2Cl_2 (500 ml) were added *N*-bromosuccinimide (NBS; 37.4 g, 210 mmol) and 100–200 mesh silica gel (20.0 g). The mixture was vigorously stirred at r.t. for 24 h. The insoluble silica gel was removed by filtration, the filter residue was washed with CH_2Cl_2 (3 × 150 ml), and the resulting org. layer was washed with H_2O (200 ml) and dried (Na_2SO_4). The solvent was removed under reduced pressure, and the crude oil was purified *via* FC (CH_2Cl_2/hexane 1:6) yield **6** (41.6 g, 96%). Clear oil. ^{1}H-NMR (300 MHz, $CDCl_3$): 7.03 (*dd*, *J* = 2.4, 8.7, 1 H); 6.97 (*d*, *J* = 2.4, 1 H); 6.73 (*d*, *J* = 8.7, 1 H); 3.86 (*s*, 3 H); 3.85 (*s*, 3 H). EI-MS: 218 ([*M*(^{81}Br)]$^+$, 50), 216 ([*M*(^{79}Br)]$^+$, 52), 203 (21), 201 (22), 94 (100), 79 (28), 63 (11), 51 (14).

(3,4-Dimethoxyphenyl)boronic Acid (**7**). To a dried three-neck round-bottom flask (1000 ml) under Ar were added **6** (32.4 g, 150 mmol) and dry THF (300 ml). The mixture was cooled to −78° and stirred under Ar for 30 min. The mixture was degassed and refilled with Ar three times. BuLi (66 ml, 2.5M, 165 mmol) was added dropwise *via* syringe. After stirring at −78° for 2 h, $B(OMe)_3$ (20 ml, 178 mmol) was added dropwise at −78°, and the mixture was allowed to warm to r.t. and stirred for 6 h. The soln. was cooled to −20°, acidified with 4N HCl to pH 2–3, and allowed to warm to r.t. The mixture was extracted with AcOEt (3 × 200 ml) and washed with brine (300 ml). The solvent was removed under reduced pressure, and the residue was redissolved in 2N NaOH soln. (100 ml). After filtration, the soln. was acidified with 4N HCl to pH 2–3. The white solid precipitated was extracted with AcOEt (3 × 300 ml) and washed with brine (300 ml). The org. layer was dried (Na_2SO_4). The solvent was concentrated under reduced pressure until precipitation of the boronic acid was observed. Excess hexane was added, and the precipitate was filtered to yield **7** (17.2 g, 63%) as a white solid, which was air-dried for a minimum time to prevent anhydride formation. M.p. 245–248° ([25]: 245–250°). ^{1}H-NMR (300 MHz, D_2O): 7.14 (*d*, *J* = 8.1, 1 H); 7.06 (*s*, 1 H); 6.77 (*d*, *J* = 7.8, 1 H); 3.64 (*s*, 3 H); 3.63 (*s*, 3 H). ESI-MS: 227 ([*M* + COOH]$^-$).

2-Bromo-3′,4′-dimethoxy-1,1′-biphenyl (**8**). To a *Schlenk* flask (1000 ml) were added 1,2-dibromobenzene (12.0 g, 66.0 mmol), **7** (19.5 g, 82.5 mmol), $Pd(PPh_3)_4$ (3.81 g, 3.3 mmol), toluene (300 ml), EtOH (200 ml), and Na_2CO_3 soln. (100 ml, 2.5M, 250 mmol). The mixture was degassed and refilled with Ar three times. The mixture was heated at reflux for 24 h. After cooling to r.t., the mixture was diluted with H_2O (300 ml), and the aq. layer was extracted with CH_2Cl_2 (3 × 200 ml). The combined org. solvent was washed with brine (200 ml), dried (Na_2SO_4), and concentrated *in vacuo*. The residue was purified by FC (CH_2Cl_2/hexane 1:3) to give **8** (16.2 g, 84%). Pale yellow oil. ^{1}H-NMR (300 MHz, $CDCl_3$): 7.66 (*d*, *J* = 8.1, 1 H); 7.32–7.33 (*m*, 2 H); 7.21–7.15 (*m*, 1 H); 6.97–6.91 (*m*, 3 H); 3.92 (*s*, 3 H); 3.90 (*s*, 3 H). EI-MS: 294 ([*M*(^{81}Br)]$^+$, 99), 292 ([*M*(^{79}Br)]$^+$,100); 277 (22), 279 (21), 170 (58), 152 (31), 139 (33), 127 (72).

2,2′-Dibromo-3′,4′-dimethoxy-1,1′-biphenyl (**4**). To a soln. of **8** (18.0 g, 62 mmol) in AcOH (100 ml) was added Br_2 (3.75 ml, 73.5 mmol) at r.t. The resulting mixture was stirred overnight before quenching the reaction with Na_2SO_3 soln. (50 ml). The aq. layer was extracted with CH_2Cl_2 (3 × 200 ml). The combined org. layer was washed with brine (200 ml), dried (Na_2SO_4), and concentrated *in vacuo*. The residue was purified by FC (CH_2Cl_2/hexane 1:3) to afford **4** (21.2 g, 92%). White solid. M.p. 111–114° ([26]: 109.9–110.8°). ^{1}H-NMR (300 MHz, $CDCl_3$): 7.67 (*d*, *J* = 8.1, 1 H); 7.38 (*t*, *J* = 7.2, 1 H); 7.29–7.23 (*m*, 2 H); 7.12 (*s*, 1 H); 6.75 (*s*, 1 H); 3.93 (*s*, 3 H); 3.86 (*s*, 3 H). EI-MS: 374 ([*M*(^{81}Br ^{81}Br)]$^+$, 54), 372 ([*M*(^{81}Br ^{79}Br)]$^+$, 100), 370 ([*M*(^{79}Br ^{79}Br)]$^+$, 52), 357 (11), 293 (10), 291 (9), 248 (17), 126 (32).

2,3,10,11-Tetramethoxy- and 2,3,6,7-Tetramethoxytetraphenylene (**10** and **11**, resp.). To a soln. of **4** (3.72 g, 10 mmol) in THF (90 ml) was added a 2.5M hexane soln. of BuLi (10 ml, 25 mmol) dropwise at −78°, and the mixture was stirred for 4 h at −78°. Then, anh. $CuCl_2$ (4.03 g, 30 mmol) was added. After stirring for 2 h at −78°, the mixture was allowed to warm to r.t. and stirred overnight. The reaction was quenched with $NH_3 \cdot H_2O$ (2N, 150 ml). The org. layer was then separated, and the aq. layer was extracted with CH_2Cl_2 (3 × 200 ml). The combined org. extracts were washed with $NaHSO_3$ (2M; 150 ml), brine (2 × 200 ml), dried (Na_2SO_4), filtered, and concentrated under reduced pressure. FC (AcOEt/CH_2Cl_2/hexane 1:2:8) gave a mixture **10**/**11**. Then, **10**/**11** was subjected to successive FC (AcOEt/CH_2Cl_2/hexane 1:10:15) afforded pure **10** and **11**, resp.

The less polar compound was **11** (440 mg, 21%). White solid. M.p. 262–264°. IR: 3445, 3055, 2994, 2933, 2844, 1602, 1510, 1479, 1462, 1436, 1395, 1383, 1333, 1320, 1256, 1233, 1202, 1170, 1154, 1051, 1025, 861, 762,748, 597. ^{1}H-NMR (300 MHz, $CDCl_3$): 7.32–7.26 (*m*, 4 H); 7.21–7.15 (*m*, 4 H); 6.68 (*s*, 2 H); 6.67 (*s*, 2 H); 3.85 (*s*, 6 H); 3.84 (*s*, 6 H). ^{13}C-NMR (100 MHz, $CDCl_3$): 147.9; 147.8; 142.0; 141.6; 134.0; 133.7; 129.24; 129.17; 127.2; 127.1; 112.3; 112.2; 55.94; 55.88. EI-MS: 424 (*M*$^+$, 100), 425 (33), 409 (5), 366 (9), 335 (12), 85 (5), 71 (4), 57 (9). HR-MS: 424.1673 (*M*$^+$, $C_{28}H_{24}O_4^+$; calc. 424.1675).

The more polar compound was **10** (236 mg, 11%). White solid. M.p. 219–222°. ^{1}H-NMR (300 MHz, $CDCl_3$): 7.29–7.24 (*m*, 4 H); 7.22–7.16 (*m*, 4 H); 6.69 (*s*, 4 H); 3.86 (*s*, 12 H). ^{13}C-NMR (100 MHz, $CDCl_3$): 147.8; 141.5; 133.9; 129.2; 127.0; 112.1; 55.8. IR: 3445, 3060, 3015,2991, 2955, 2932, 2844, 1735, 1606, 1539, 1516, 1483, 1463, 1434, 1383, 1353, 1259, 1235, 1204, 1184, 1166, 1049, 1025, 859, 817, 772, 757, 738, 639, 608, 567. EI-MS: 424 (*M*$^+$, 100), 425 (33), 409 (5), 366 (9), 335 (12), 85 (5), 71 (4), 57 (9). HR-MS: 424.1671 (*M*$^+$, $C_{28}H_{24}O_4^+$; calc. 424.1675).

Tetraphenylene-2,3,10,11-tetrol (**1**). To a vigorously stirred suspension of **10** (424 mg, 1 mmol) in CH_2Cl_2 (100 ml) at 0° was added a 1.0M soln. of BBr_3 in CH_2Cl_2 (10 ml, 10 mmol) slowly. The mixture was stirred overnight at r.t., and a clear brownish-red soln. was obtained. The mixture was hydrolyzed by careful addition of cold H_2O (10 ml), and the white solid precipitated was dissolved by addition of AcOEt (100 ml). The org. layer was separated, and the aq. layer was extracted with AcOEt (2 × 50 ml). The combined org. extract was dried (Na_2SO_4) and evaporated under reduced pressure. The residue was purified by FC (hexane/AcOEt 1:1) to give **1** (411 mg, 98%). Air- and moisture-sensitive white solid. M.p. 356–362°. IR: 3494, 3364, 3273, 3057, 1606, 1522, 1486, 1448, 1423, 1355, 1292, 1272, 1240, 1224, 1211, 1190, 1159, 891, 878, 868, 830, 767, 633, 579, 568. ^{1}H-NMR (300 MHz, CD_3COCD_3): 7.97 (br., 4 H); 7.23–7.20 (*m*, 4 H); 7.11–7.08 (*m*, 4 H); 6.62 (*s*, 4 H). ^{13}C-NMR (100 MHz, CD_3OD): 145.6; 143.6; 135.4; 130.3; 127.9; 117.3. ESI-MS: 367 ([*M* − H]$^-$), 403 ([*M* + C_2H_5OH − H]$^-$). HR-MS: 391.09475 ([*M* + Na]$^+$, $C_{28}H_{24}NaO_4^+$; calc. 391.09408.

Tetraphenylene-2,3,6,7-tetrol (**12**). To a soln. of **10**/**11** (551 mg, 1.3 mmol) in CH_2Cl_2 (150 ml) at 0° was added a 1.0M soln. of BBr_3 in CH_2Cl_2 (12 ml, 12 mmol) slowly. The mixture was stirred overnight at

r.t., and a clear brownish-red soln. was obtained. The mixture was hydrolyzed by careful addition of cold H_2O (10 ml), and the resulting white precipitate was dissolved by the addition of AcOEt (100 ml). The org. layer was separated, and the aq. layer was extracted with AcOEt (2 × 50 ml). The combined org. extract was dried (Na_2SO_4) and evaporated under reduced pressure to provide a white solid. Then, the white solid was washed by CH_2Cl_2 (100 ml × 5), the combined filtrate was evaporated under reduced pressure to afford a tan oil, and recrystallization from EtOH gave **12**. Off-white solid. M.p. 353–358°. IR: 3395, 3080, 2975, 2888, 1617, 1599, 1521, 1480, 1455, 1422, 1383, 1353, 1286, 1266, 1223, 1202, 1182, 1148, 1087, 1033, 878, 871, 838, 827, 761, 749. ^{1}H-NMR (300 MHz, CD_3COCD_3, [**12** · 3 E*t*OH]): 7.92 (*s*, 4 H); 7.26–7.22 (*m*, 4 H); 7.13–7.07 (*m*, 4 H); 6.62 (*s*, 2 H); 6.61 (*s*, 2 H); 3.40 (*q*, *J* = 6.9, 6 H); 1.11 (*t*, *J* = 6.9, 9 H). ^{13}C-NMR (100 MHz, CD_3COCD_3, [**12** · 3 CH_3CH_2OH]: 144.1; 143.9; 142.2; 142.1; 133.6; 133.5; 129.0; 128.8; 127.0; 126.7; 116.1; 115.9; 65.2; 14.7. ESI-MS: 367 ([*M* − H]$^-$), 403 ([*M* + C_2H_5OH − H]$^-$). HR-MS: 391.09335 ([*M* + Na]$^+$, $C_{24}H_{16}Na^+O_4^+$; calc. 391.09408). The filter residue was further purified by FC (hexane/AcOEt 1:1) to afford **1**.

(3′,4′-Dimethoxy[1,1′-biphenyl]-2-yl)boronic Acid (**14**). To a dried three-neck round-bottom flask (1000 ml) under Ar were added **8** (14.6 g, 50 mmol) and dry THF (150 ml). The mixture was cooled to − 78° and stirred under Ar for 30 min. The mixture was degassed and refilled with Ar three times. BuLi (22 ml; 2.5M, 55 mmol) was added dropwise *via* syringe. After stirring at − 78° for 2 h, $B(OMe)_3$ (7 ml, 60 mmol) was added dropwise at − 78°, and the mixture was allowed to warm to r.t. and stirred for 4 h. The soln. was cooled to − 20°, acidified with 4N HCl to pH 2–3, and allowed to warm to r.t. The mixture was extracted with AcOEt (3 × 200 ml), washed with brine (300 ml), and dried (Na_2SO_4). The solvent was removed under reduced pressure and the residue was purified by FC (AcOEt/hexane 1:1) to give **14** (6.07 g, 89%). White solid. M.p. 270–273°. IR: 3484, 3366, 3069, 2954, 2927, 2832, 1606, 1588, 1561, 1520, 1460, 1437, 1381, 1340, 1259, 1240, 1211, 1021, 848, 812, 772, 755, 649, 634. ^{1}H-NMR (400 MHz, $CDCl_3$): 7.92 (*dd*, *J* = 1.2, 7.6, 1 H); 7.46 (*td*, *J* = 1.6, 7.6, 1 H); 7.38 (*td*, *J* = 1.2, 7.6, 1 H); 7.30 (*dd*, *J* = 0.4, 7.6, 1 H); 6.94 (*s*, 2 H); 6.91 (*s*, 1 H); 3.92 (*s*, 3 H); 3.88 (*s*, 3 H). ^{13}C-NMR (100 MHz, $CDCl_3$): 148.8; 148.7; 146.9; 135.1; 135.0; 130.3; 129.3; 126.7; 120.8; 111.9; 111.1; 55.80; 55.78. ESI-MS: 303 ([*M* + HCOO]$^-$). HR-MS: 281.0862 ([*M* + Na]$^+$, $C_{14}H_{15}BNaO_4^+$; calc. 281.0956).

(2′-Bromo-4′,5′-dimethoxy[1,1′-biphenyl]-2-yl)boronic Acid (**13**). To a soln. of **14** (2.58 g, 10 mmol) in EtOH (40 ml) were added NBS (1.96 g, 11 mmol) and 100–200-mesh silica gel (4.0 g). The mixture was vigorously stirred at r.t. for 12 h. The insoluble silica gel was removed by filtration, the filter residue was washed three times with AcOEt (3 × 100 ml), and the resulting org. layer was washed two times with H_2O (2 × 50 ml) and dried (Na_2SO_4). The solvent was removed under reduced pressure, and the residue was purified by FC (AcOEt/hexane 2:3) to give **13** (3.20 g, 95%). White solid. M.p. 112–115°. IR: 3432, 3343, 3007, 2970, 2936, 2839, 1598, 1560, 1506, 1478, 1459, 1436, 1394, 1379, 1338, 1247, 1230, 1203, 1166, 1085, 1018, 859, 791, 771, 649. ^{1}H-NMR (300 MHz, (D_6)DMSO): 7.72 (*s*, 2 H); 7.56 (*d*, *J* = 6.6, 1 H); 7.41–7.29 (*m*, 2 H); 7.20 (*d*, *J* = 7.5, 1 H); 7.15 (*s*, 1 H); 6.92 (*s*, 1 H); 3.80 (*s*, 3 H); 3.73 (*s*, 3 H). ^{13}C-NMR (75 MHz, (D_6)DMSO): 148.9; 148.2; 144.9; 136.6; 133.3; 130.2; 128.7; 126.9; 115.9; 115.4; 112.0; 56.5; 56.3. EI-MS: 338 ([*M*(^{81}Br)]$^+$, 98), 336 ([*M*(^{79}Br)]$^+$, 100), 256 (46), 242 (66), 241 (39), 227 (70), 226 (44), 126 (51). Anal. calc. for $C_{14}H_{14}BBrO_4$: C 49.90, H 4.19; found: C 49.91, H 4.16.

Cyclic Dimerization of **13** *under* Suzuki *Coupling Reaction Condition.* To a *Schlenk* flask (25 ml) were added **13** (100 mg, 0.3 mmol), $Pd(PPh_3)_4$ (70 mg, 0.06 mmol), 1,2-dimethoxyethane (DME; 15 ml), and K_2CO_3 soln. (0.75 ml, 2.0M, 1.5 mmol). The mixture was degassed and refilled with Ar three times and heated at reflux for 10 h. After cooling to r.t., the mixture was diluted with H_2O (15 ml), and the aq. layer was extracted with CH_2Cl_2 (3 × 50 ml). The combined org. solvent was dried (Na_2SO_4), and concentrated *in vacuo*. The residue was purified by FC (AcOEt/CH_2Cl_2/hexane 1:10:15 and then 1:2:6) to give **10**/**11** (18 mg, 28%; *ca.* 1:1 by ^{1}H-NMR), together with the following two considerably air- and moisture-stable intermediates:

The less polar intermediate was *bis(triphenylphosphine)(4,5-dimethoxy-[1,1′-biphenyl]-2-yl)palladium(II) bromide* (**15**). Pale yellow solid. M.p. 219–221°. IR: 3051, 3002, 2932, 2831, 1585, 1549, 1479, 1433, 1359, 1236, 1195, 1164, 1094, 1071, 1019, 998, 850, 781, 763, 744, 692,519, 494. ^{1}H-NMR (400 MHz, (D_6)DMSO): 7.43–7.39 (*m*, 8 H); 7.56 (*t*, *J* = 7.2, 13 H); 7.22–7.19 (*m*, 14 H); 6.30 (*s*, 1 H); 6.27 (*s*, 1 H); 3.52 (*s*, 3 H); 3.08 (*s*, 3 H). ^{31}P-NMR (121 MHz, $CDCl_3$): 22.5. ESI-MS: 843.1 ([*M* − Br]$^+$). Anal. calc. for $C_{50}H_{43}BrO_2P_2Pd$: C 64.98, H 4.69; found: C 64.82, H 4.88.

The less polar intermediate was *bis(triphenylphosphine)(3′,4′-dimethoxy-[1,1′-biphenyl]-2-yl)palladium(II) bromine* (**16**). Pale-yellow solid. M.p. 217–220°. IR: 3053, 2999, 2952, 2831, 1571, 1514, 1479, 1463, 1433, 1399, 1270, 1249, 1234, 1170, 1135, 1093, 1024, 998, 866, 743, 732, 692, 518, 498. ^{1}H-NMR (400 MHz, (D_6)DMSO): 7.63 (*dd*, *J* = 2.0, 8.0, 1 H); 7.41 (*t*, *J* = 7.6, 6 H); 7.28 (*t*, *J* = 7.6, 12 H); 7.25–7.18 (*m*, 12 H); 6.94–6.91 (*m*, 1 H); 6.89 (*d*, *J* = 7.6, 1 H); 6.63–6.57 (*m*, 2 H); 6.33 (*t*, *J* = 8.0, 1 H); 6.24 (*d*, *J* = 2.0, 1 H); 3.52 (*s*, 3 H); 3.08 (*s*, 3 H). ^{31}P-NMR (121 MHz, $CDCl_3$): 22.2. ESI-MS: 843.1 ($[M-Br]^+$). Anal. calc. for $C_{50}H_{43}BrO_2P_2Pd$: C 64.98, H 4.69; found: C 64.782, H 4.82.

2,2′-[1,2-Phenylenebis(oxy-2,1-ethanediyloxy-2,1-ethanediyloxy)]bisethanol (**23**). To a flask (250 ml) filled with Ar were added *catechol* (**20**; 3.63 g, 33 mmol), *8-(tosyloxy)-3,6-dioxaoctanol* (**22**; 9.12 g, 30 mmol), K_2CO_3 (9.11 g, 66 mmol), and acetone (400 ml). The mixture was heated to 90° and stirred under Ar for 24 h, filtered through a small pad of silica gel, and then washed with acetone. The solvent was evaporated under reduced pressure, and the residue was purified by FC (AcOEt/hexane 1:1 and then acetone) to give **23** (4.53 g, 73%). Pale-yellow oil. ^{1}H-NMR (300 MHz, $CDCl_3$): 6.92 (*s*, 4 H); 4.18 (*t*, *J* = 5.1, 4 H); 3.88 (*t*, *J* = 4.8, 4 H); 3.78–3.67 (*m*, 12 H); 3.60 (*t*, *J* = 4.8, 4 H); 3.34 (br., 2 H). ESI-MS: 375 ($[M+H]^+$), 392 ($[M+NH_4]^+$), 397 ($[M+Na]^+$).

Benzene-1,2-diylbis(oxyethane-2,1-diyloxyethane-2,1-diyloxyethane-2,1-diyl) Bis(4-methylbenzenesulfonate) (**24**). To a soln. of **23** (3.74 g, 10 mmol) in dried CH_2Cl_2 (100 ml) were added Ag_2O (5.78 g, 25 mmol), TsCl (5.72 g, 30 mmol), and KI (415 mg, 2.5 mmol). The mixture was stirred at r.t. for 24 h, filtered through a small pad of silica gel, and then washed with AcOEt. The solvent was evaporated under reduced pressure, and the residue was purified by FC (AcOEt/hexane 3:1) to give **24** (6.07 g, 89%). Pale-yellow oil. ^{1}H-NMR (300 MHz, $CDCl_3$): 7.79 (*d*, *J* = 8.1, 4 H); 7.33 (*d*, *J* = 8.4, 4 H); 6.91 (*s*, 4 H); 4.16–4.11 (*m*, 8 H); 3.83 (*t*, *J* = 5.1, 4 H); 3.71–3.66 (*m*, 8 H); 3.62–3.59 (*m*, 4 H); 2.43 (*s*, 6 H). ESI-MS: 683 ($[M+H]^+$), 700 ($[M+NH_4]^+$), 705 ($[M+Na]^+$).

Tweezer-Shaped Host **2**. A suspension of K_2CO_3 (1.66 g, 12 mmol) in MeCN (150 ml) under Ar was stirred vigorously for 15 min and then heated to 100°. To the mixture were added dropwise a soln. of **1** (442 mg, 1.2 mmol) and **24** (1.71 g, 2.5 mmol) in MeCN (150 ml) and acetone (30 ml) over 12 h. The mixture was stirred at 100° for another 96 h. After cooling to r.t., the mixture was filtered and washed with CH_2Cl_2 (200 ml). The filtrate was removed under reduced pressure to give a pale tan oil, which was redissolved in CH_2Cl_2 (100 ml) and washed with H_2O (2 × 50 ml). The org. layer was dried ($MgSO_4$). After removal of the solvent, the resulting oil was subjected to successive FC (CH_2Cl_2/MeOH 100:1 and then 60:1) to afford **2** (480 mg, 38%). White solid. M.p. 64–72°. IR: 3445, 2923, 2869, 1594, 1506, 1480, 1455, 1435, 1351, 1333, 1257, 1181, 1127, 1055, 947, 746, 614. ^{1}H-NMR (300 MHz, $CDCl_3$/CD_3CN): 7.27–7.22 (*m*, 4 H); 7.14–7.11 (*m*, 4 H); 6.88 (*s*, 8 H); 6.66 (*s*, 4 H); 4.18–4.03 (*m*, 16 H); 3.83–3.81 (*m*, 16 H); 3.72 (*s*, 16 H). ^{13}C-NMR (100 MHz, $CDCl_3$): 148.9; 147.7; 141.5; 134.5; 129.2; 127.0; 121.4; 114.6; 114.0; 71.3; 69.9; 69.8; 69.44; 69.39. ESI-MS: 1067.5 ($[M+Na]^+$), 1083.5 ($[M+K]^+$). MALDI-MS: 1067.4 ($[M+Na]^+$), 1083.4 ($[M+K]^+$). HR-MS: 1067.4421 ($[M+Na]^+$, $C_{60}H_{68}NaO_{16}^+$; calc. 1067.4399). Anal. calcd. for $C_{60}H_{68}O_{16}\cdot 0.5\ H_2O$: C 68.36, H 6.60; found: C 68.29, H 6.61.

X-Ray Crystal-Structure Determination. The crystal of **10** belongs to the orthorhombic crystal system, space group *Pnma* with *a* = 17.599(3), *b* = 17.435(3), *c* = 8.8206(13) Å, $\alpha=\beta=\gamma=90°$, *V* = 2706.5(7) Å^3, ϱ_{calc} = 1.335 Mg/m^3, λ = 0.71073 Å (MoK_α), μ = 0.371 mm^{-1}, *F*(000) = 1128, and *T* 293(2) K. Data collection yielded 14066 reflections resulting in 2752 unique, averaged reflections, 1990 with $I > 2\sigma(I)$, θ range 2.31–26.00°. Full-matrix least-squares refinement led to a final *R* = 0.0597, *wR* = 0.1693, and g.o.f. = 1.054. The diffraction measurement was carried out on a *Bruker Smart Apex* and *CCD* area detector. CCDC-896135 contains the supplementary crystallographic data for the structure of **10**[2]).

The crystal of **15** belongs to the triclinic crystal system, space group *P*1 with *a* = 10.6486(11), *b* = 11.3972(11), *c* = 19.742(2) Å, α = 74.836(2), β = 83.552(2), γ = 67.208(2)°, *V* = 2131.8(4) Å^3, ϱ_{calc} = 1.440 Mg/m^3, λ = 0.71073 Å (MoK_α), μ = 1.487 mm^{-1}, *F*(000) = 940, and *T* 133(2) K. Data collection yielded 17334 reflections resulting in 9748 unique, averaged reflections, 8511 with $I > 2\sigma(I)$, θ range 1.07–27.56°. Full-matrix least-squares refinement led to a final *R* = 0.0306, *wR* = 0.1165, and

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[2]) Supplementary crystallographic data can be obtained free of charge *via* http://www.ccdc.cam.ac.uk/data_request/cif.

g.o.f. = 0.913. The diffraction measurement was carried out on a *Bruker Apex-II CCD* diffractometer. CCDC-896085 contains the supplementary crystallographic data for the structure of **15**[2]).

The crystal of **16** belongs to the triclinic crystal system, space group $P\bar{1}$ with $a = 11.4043(14)$, $b = 14.1702(18)$, $c = 14.7445(19)$ Å, $\alpha = 96.239(3)$, $\beta = 92.989(4)$, $\gamma = 90.137(3)^\circ$, $V = 2365.3(5)$ Å^3, $\varrho_{calc} = 1.465$ Mg/m^3, $\lambda = 0.71073$ Å (MoK_α), $\mu = 1.513$ mm^{-1}, $F(000) = 1056$, and T 293(2) K. Data collection yielded 13753 reflections resulting in 8764 unique, averaged reflections, 4448 with $I > 2\sigma(I)$, θ range 1.79–25.50°. Full-matrix least-squares refinement led to a final $R = 0.0784$, $wR = 0.1584$, and g.o.f. = 0.921. The diffraction measurement was carried out on a *Bruker Smart Apex* and *CCD* area detector. CCDC-896084 contains the supplementary crystallographic data for the structure of **16**[2]).

REFERENCES

[1] J.-M. Lehn, 'Supramolecular Chemistry Concepts and Perspectives', Wiley-VCH, Weinheim, 1995; J. L. Atwood, J. W. Steed, 'Supramolecular Chemistry', Wiley-VCH, Weinheim, 2000; J. W. Steed, J. L. Atwood, 'Supramolecular Chemistry', John Wiley & Sons, Hoboken, 2009; J. L. Atwood, J. E. D. Davies, D. D. MacNicol, F. Vogtle, J.-M. Lehn, 'Comprehensive Supramolecular Chemistry', Elsevier, The Netherlands, 1996.

[2] S. M. Biros, J. Rebek Jr., *Chem. Soc. Rev.* **2007**, *36*, 93; S. O. Kang, J. M. Llinares, V. W. Day, K. Bowman-James, *Chem. Soc. Rev.* **2010**, *39*, 3980; Y. Liu, Y. Chen, *Acc. Chem. Res.* **2006**, *39*, 681; J. S. Kim, S. Y. Lee, J. Yoon, J. Vicens, *Chem. Commun.* **2009**, 4791; M. J. Frampton, H. L. Anderson, *Angew. Chem., Int. Ed.* **2007**, *46*, 1028; K. Kim, N. Selvapalam, Y. H. Ko, K. M. Park, D. Kim, J. Kim, *Chem. Soc. Rev.* **2007**, *36*, 267; L. Isaacs, *Chem. Commun*. **2009**, 619; P. A. Gale, P. Anzenbacher Jr., J. L. Sessler, *Coord. Chem. Rev.* **2001**, *222*, 57; P. A. Gale, *Chem. Soc. Rev.* **2010**, *39*, 3746; M. Albrecht, P. Stortz, *Chem. Soc. Rev.* **2005**, *34*, 496.

[3] W. S. Rapson, R. G. Shuttleworth, J. N. Niekerk, *J. Chem. Soc.* **1943**, 326.

[4] H. Irngartinger, W. R. K. Reibel, *Acta Crystallogr., Sect. B* **1981**, *37*, 1724.

[5] T. C. W. Mak, H. N. C. Wong, in 'Comprehensive Supramolecular Chemistry', Eds. D. D. MacNicol, F. Toda, P. Bishop, Pergamon Press, Oxford, 1996, Vol. 6, p. 351; T. C. W. Mak, H. N. C. Wong, *Top. Curr. Chem.* **1987**, *140*, 141; X.-L. Hou, H. Huang, H. N. C. Wong, *Synlett* **2005**, 1073; A. Rajca, S. Rajca, M. Pink, M. Miyasaka, *Synlett* **2007**, 1799; I. Hisaki, M. Sonoda, Y. Tobe, *Eur. J. Org. Chem.* **2006**, 833; C. Wang, Z. Xi, *Chem. Commun.* **2007**, 5119; M. J. Marsella, S. Rahbarnia, N. Wilmot, *Org. Biomol. Chem.* **2007**, *5*, 391; H. Huang, C.-K. Hau, C. C. M. Law, H. N. C. Wong, *Org. Biomol. Chem.* **2009**, *7*, 1249; S. M. Bachrach, *J. Org. Chem.* **2009**, *74*, 3609; A. Rajca, S. Rajca, *Angew. Chem., Int. Ed.* **2010**, *39*, 672.

[6] G. Wittig, G. Lehmann, *Chem. Ber.* **1957**, *90*, 875; G. Wittig, G. Klar, *Liebigs Ann. Chem.* **1967**, *704*, 91; G. Wittig, F. Bickelhaupt, *Chem. Ber.* **1958**, *91*, 883; H. J. S. Winkler, G. Wittig, *J. Org. Chem.* **1963**, *28*, 1733; G. Wittig, *Q. Rev., Chem. Soc.* **1966**, *20*, 191.

[7] D. Hellwinkel, G. Reiff, V. Nykodym, *Liebigs Ann. Chem.* **1977**, 1013.

[8] O. Puglisi, F. A. Bottino, A. Recca, J. K. Stille, *J. Chem. Res., Synop.* **1980**, 216.

[9] A. Rajca, H. Wang, P. Bolshov, S. Rajca, *Tetrahedron* **2001**, *57*, 3725; S. M. H. Kabir, M. Hasegawa, Y. Kuwatani, M. Yoshida, H. Matsuyama, M. Iyoda, *J. Chem. Soc., Perkin Trans. 1* **2001**, 159; A Rajca, A. Safronov, S. Rajca, J. Wongsriratanakul, *J. Am. Chem. Soc.* **2000**, *122*, 3351.

[10] J. Chatt, R. G. Guy, H. R. Watson, *J. Chem. Soc.* **1961**, 2332; J. J. Eisch, A. M. Piotrowski, K. I. Han, C. Krüger, Y. H. Tsay, *Organometallics* **1985**, *4*, 224; H. Schwager, S. Spyroudis, K. P. C. Vollhardt, *J. Organomet. Chem*. **1990**, *382*, 191; B. L. Edelbach, R. J. Lachicotte, W. D. Jones, *J. Am. Chem. Soc*. **1998**, *120*, 2843.

[11] H. N. C. Wong, F. Sondheimer, *Tetrahedron* **1981**, *37*, 99; Y. D. Xing, N. Z. Huang, *J. Org. Chem.* **1982**, *47*, 140.

[12] T. Shibata, T. Chiba, H. Hirashima, Y. Ueno, K. Endo, *Angew. Chem., Int. Ed.* **2009**, *48*, 8066.

[13] D. Hellwinkel, G. Reiff, *Angew. Chem., Int. Ed.* **1970**, *9*, 527; T. Kauffmann, *Angew. Chem., Int. Ed.* **1979**, *18*, 1.

[14] R. Rathore, P. L. Magueres, S. V. Lindeman, J. K. Kochi, *Angew. Chem., Int. Ed.* **2000**, *39*, 809; H. Ishikawa, I. Higashiguchi, H. Tada, Y. Morioka, A. Oda, Jpn. Pat. 2001-167884, 2001; J. Ogasawara, T. Igarashi, S. Sano, U.S. Pat. 2005/0112407, 2005; M. Watanabe, T. Ohashi, Jpn. Pat. 2007-210964, 2007; M. Watanabe, T. Ohashi, Jpn. Pat. 2007-250784, 2007.
[15] E. Wuckert, M. Dix, S. Laschat, A. Baro, J. L. Schulte, C. Hägele, F. Giesselmann, *Liq. Cryst.* **2004**, *31*, 1305; E. Wuckert, S. Laschat, A. Baro, C. Hägele, F. Giesselmann, H. Luftmann, *Liq. Cryst.* **2006**, *33*, 103; C. Hägele, E. Wuckert, S. Laschat, F. Giesselmann, *ChemPhysChem* **2009**, *10*, 1291; E. Wuckert, C. Hägele, F. Giesselmann, A. Baro, S. Laschat, *Beilstein J. Org. Chem.* **2009**, *5*, 57.
[16] C.-K. Hau, S. S.-Y. Chui, W. Lu, C.-M. Che, P.-S. Cheng, T. C. W. Mak, Q. Miao, H. N. C. Wong, *Chem. Sci.* **2011**, *2*, 1068.
[17] a) J.-F. Wen, W. Hong, K. Yuan, T. C. W. Mak, H. N. C. Wong, *J. Org. Chem.* **2003**, *68*, 8918; b) H.-Y. Peng, C.-K. Lam, T. C. W. Mak, Z. Cai, W.-T. Ma, Y.-X. Li, H. N. C. Wong, *J. Am. Chem. Soc.* **2005**, *127*, 9603; c) F. Lin, H.-Y. Peng, J.-X. Chen, D. T. W. Chik, Z. Cai, K. M. C. Wong, V. W. W. Yam, H. N. C. Wong, *J. Am. Chem. Soc.* **2010**, *132*, 16383.
[18] A. Sygula, F. R. Fronczek, R. Sygula, P. W. Rabideau, M. M. Olmstead, *J. Am. Chem. Soc.* **2007**, *129*, 3842.
[19] C.-K. Hau, H. He, A. W. M. Lee, D. T. W. Chik, Z. Cai, H. N. C. Wong, *Tetrahedron* **2010**, *66*, 9860.
[20] a) C. W. Lai, K. Chi, K. Hung, T. C. W. Mak, H. N. C. Wong, *Org. Lett.* **2003**, *5*, 823; b) C. W. Hui, T. C. W. Mak, H. N. C. Wong, *Tetrahedron* **2004**, *60*, 3523; c) A.-H. Wu, C.-K. Hau, H. N. C. Wong, *Adv. Synth. Catal.* **2007**, *349*, 601; d) J.-F. Cui, H. Huang, H. N. C. Wong, *Synlett* **2011**, *7*, 1018; e) H. Huang, S. Stewart, M. Gutmann, T. Ohhara, N. Niimura, Y.-X. Li, J.-F. Wen, R. Bau, H. N. C. Wong, *J. Org. Chem.* **2009**, *74*, 359.
[21] F. Klärner, B. Kahlert, *Acc. Chem. Res.* **2003**, *36*, 919; M. Harmata, *Acc. Chem. Res.* **2004**, *37*, 862.
[22] a) T. Han, C.-F. Chen, *Org. Lett.* **2006**, *8*, 1069; b) X.-X. Peng, H.-Y. Lu, T. Han, C.-F. Chen, *Org. Lett.* **2007**, *8*, 895.
[23] C.-F. Chen, *Chem. Commun.* **2011**, *47*, 1674.
[24] H. Konishi, K. Aritomi, T. Okano, J. Kiji, *Bull. Chem. Soc. Jpn*. **1989**, *62*, 591.
[25] B. M. Rosen, D. A. Wilson, C. J. Wilson, M. Peterca, B. C. Won, C. Huang, L. R. Lipski, X. Zeng, G. Ungar, P. A. Heiney, V. Percec, *J. Am. Chem. Soc.* **2009**, *131*, 17500.
[26] I. Nagao, M. Shimizu, T. Hiyama, *Angew. Chem., Int. Ed.* **2009**, *48*, 7573.
[27] a) A. Suzuki, *Pure Appl. Chem.* **1991**, *63*, 419; b) N. Miyaura, A. Suzuki, *Chem. Rev.* **1995**, *95*, 2457; c) A. Suzuki, *J. Organomet. Chem.* **1999**, *576*, 147.
[28] H.-J. Zhang, J. Wei, F. Zhao, Y. Liang, Z. Wang, Z. Xi, *Chem. Commun.* **2010**, *46*, 7439.
[29] J. Tsuji, 'Palladium Reagents and Catalysts', Wiley, New York, 1995; M. Catellani, E. Motti, N. Della Ca', R. Ferraccioli, *Eur. J. Org. Chem.* **2007**, 4153.
[30] X.-Z. Zhu, C.-F. Chen, *J. Am. Chem. Soc.* **2005**, *127*, 13158.
[31] Z.-Q. Wu, X.-B. Shao, C. Li, J.-L. Hou, K. Wang, X.-K. Jiang, Z.-T. Li, *J. Am. Chem. Soc.* **2005**, *127*, 17460; F. P. Ballistreri, A. Pappalardo, G. A. Tomaselli, R. M. Toscano, G. Trusso Sfrazzetto, *Eur. J. Org. Chem.* **2010**, 3806.
[32] R. E. Heath, G. M. Dykes, H. Fish, D. K. Smith, *Chem. – Eur. J.* **2003**, *9*, 850.

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