A Simple and Versatile Synthesis of 1,2-Diarylacenaphthylenes via Suzuki–Miyaura Coupling, and its Application in the Synthesis of a New Acenaphthylene-1,2-bis(*p*-quinone methide) Derivative

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Abstract: 1,2-Diaryl-substituted acenaphthylene derivatives were prepared simply via Suzuki–Miyaura coupling in good or excellent yields. By applying this method, acenaphthylene-1,2-bis(*p*-quinone methide) with two 3,5-di-*tert*-butyl-4-oxocyclohexadienylidene units, which is a stable deep purple crystalline substance with a very broad absorption in the whole visible region and relatively low reduction potential, was prepared and characterized.

Key words: arenes, chromophores, cross-coupling, quinines, Suzuki reaction

Acenaphthylene is one of the most fundamental molecules in the family of cyclopentene-fused polycyclic aromatic hydrocarbons (CPAH). A large number of derivatives have been prepared; these have recently attracted interest as synthetic intermediates for curve-shaped PAHs[1] and also in the preparation of aryl-substituted ladder-type CPAHs.[2] Several 1,2-diaryl-substituted acenaphthylenes **1** have been reported, but most of the syntheses were multistep procedures beginning with nucleophilic addition of arylmetals (ArLi or ArMgBr) to 1,2-acenaphthenquinone, and the total yields were not high.[3] During the course of our recent studies concerning novel nonplanar extended quinonoid systems,[4] we planned to prepare the extended acenaphthenequinone **3** via oxidation of the bisphenol-substituted acenaphthylene **2** (Figure 1). A synthetic study of **2** revealed that 1,2-diarylacenaphthylenes could be prepared efficiently via Suzuki–Miyaura coupling using 1,2-dibromoacenaphthylene (**4**) as a starting material.

Although there are numerous examples of aryl–aryl bond formation from aryl halides (ArX) by transition-metal-catalyzed cross-coupling,[5] syntheses using **4** have not yet been reported.[6,7] Therefore, we examined Suzuki–Miyaura coupling of **4** with arylboronic acids (Scheme 1). Compound **4** was readily prepared by bromination of acenaphthylene with *N*-bromosuccinimide.[8]

The reaction of **4** with 3.0 equivalents of phenylboronic acid was attempted using $Pd(PPh_3)_4$ as a catalyst and aqueous K_2CO_3 as a base under refluxing DME for 18 hours. After a typical workup, 1,2-diphenylacenaphthylene (**1a**) was isolated in 85% yield. We also examined the reaction of **4** with several arylboronic acids under the same conditions; the results are shown in Table 1.

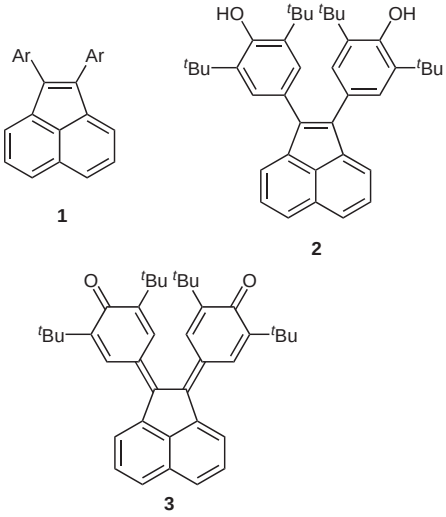
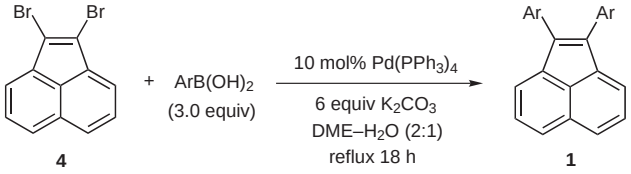


Figure 1

As shown in Table 1, various 1,2-diarylacenaphthylene derivatives were prepared in good or excellent yields.



Scheme 1 Synthesis of **1** via Suzuki–Miyaura coupling.

Table 1 Suzuki–Miyaura Coupling of **4** with Arylboronic Acids

Entry	Ar	Yield of **1** (%)
1	Ph	85 (**1a**)
2	4-$MeOC_6H_4$	96 (**1b**)
3	4-FC_6H_4	82 (**1c**)
4	2-Thienyl	94 (**1d**)
5	2-MeC_6H_4	93 (**1e**)
6	1-Naphthyl	87 (**1f**)

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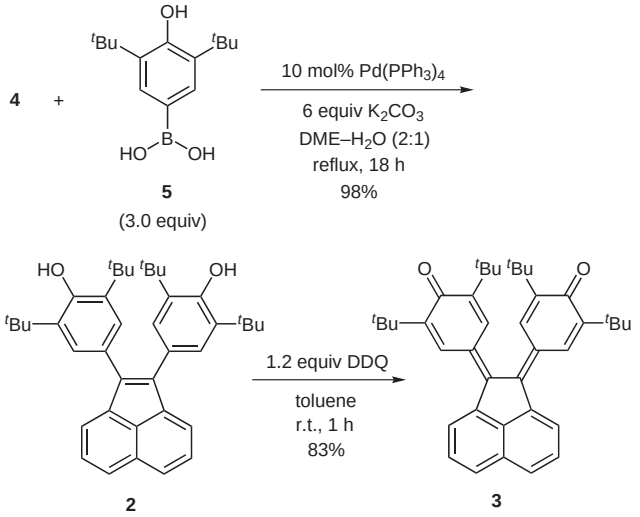
Electron-rich and electron-poor aromatic rings, as well as heteroaromatic rings, were introduced successfully (entries 2, 3, and 4). It is noteworthy that *ortho*-substituted arylboronic acids, such as 2-methylphenylboronic acid and 1-naphthylboronic acid, reacted cleanly to afford the coupling products **1e** and **1f**, respectively (entries 5 and 6).[9] Taking into account the high availability of arylboronic acids, this is, to our knowledge, the most efficient way of preparing 1,2-diarylacenaphthylenes, with few steps and high chemical yields.



Scheme 2 Synthesis of bisphenol **2** and quinone **3**.

On the basis of these results, the synthesis of bisphenol **2** was carried out using 3,5-di-*tert*-butyl-4-hydroxyphenylboronic acid (**5**).[10] Compound **2** was obtained as reddish-orange crystals in 98% yield. Successive oxidation of **2** by DDQ in toluene at room temperature for 1 hour afforded quinone **3** in 86% yield (Scheme 2).

Compound **3** is a dark-purple crystalline substance with thermal and air stability. The molecular structure of **3** was determined by X-ray crystallographic analysis (Figure 2).[12] Two independent molecules are present in the unit cell; these are stacked head-to-tail at the acenaphthene moieties to form a dimer structure, and the distance at the dimer is 3.57 Å. The acenaphthylene skeleton is almost planar, and the averaged dihedral angle of the two pinch bonds is 29.9°. The pinch bonds are twisted in a range between 11.2° and 30.6° in order to avoid steric crowding around the quinone methide units.

Sharp and well-resolved signals were observed in the ^{1}H NMR spectrum of **3**, which reflected negligible contribution of the diradical structure in **3**. At room temperature, the quinone methide protons and the *tert*-butyl protons are observed as a set of doublets (δ = 8.19 and 7.14 ppm, J = 2.0 Hz) and two singlets (δ = 1.46 and 1.21 ppm), respectively. The rotational barrier of the pinch bonds was estimated to be 17.4 kcal/mol by variable-temperature NMR measurements based on the coalescence of the *tert*-butyl protons.[13]

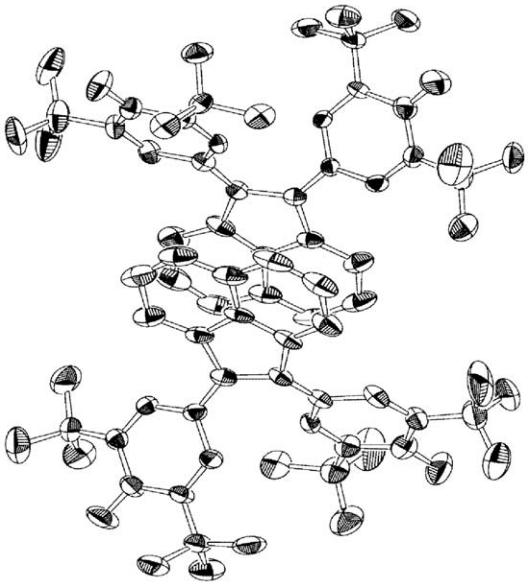


Figure 2 ORTEP drawing of unit cell of **3** (50% thermal ellipsoids). Hydrogen atoms are omitted for clarity.

The UV/Vis spectra of **2** and **3** in cyclohexane are shown in Figure 3. While compound **2** has a strong absorption maximum at λ = 238 nm (log ε = 4.74) and a weak absorption around λ = 458 nm (log ε = 3.52), compound **3** has relatively high absorbance in the whole visible region, and therefore its color in concentrated solution is nearly black.

The redox properties of these compounds were studied using cyclic voltammetry.[14] Two sets of reversible reduction waves were observed for **3** on electronic reduction ($^1E_{1/2}$ = –0.81V, $^2E_{1/2}$ = –1.19 V, vs. Fc/Fc$^+$), which indicates formation of an anion radical and a dianion. Due to π-extension, these reduction potentials are much lower than those of 1,2-acenaphthenequinone ($^1E_{1/2}$ = –1.35 V, $^2E_{1/2}$ = –2.33 V, vs. Fc/Fc$^+$). This redox behavior is similar to that of pyracylene-extended quinone **6**.[4e] The

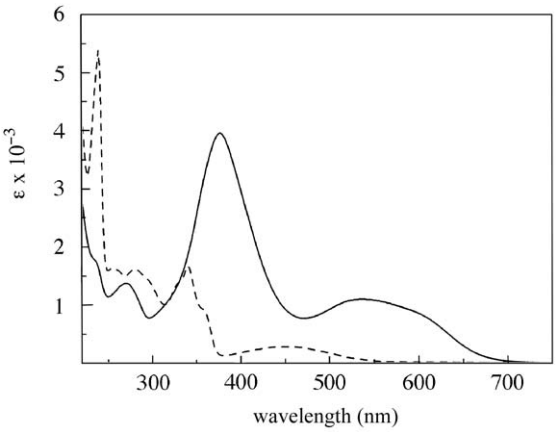


Figure 3 UV/Vis spectra of **2** (dashed line) and **3** (solid line) in cyclohexane.

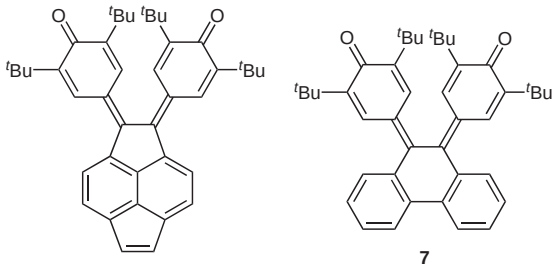


Figure 4

reversibility is attributed to its rigid structure, similarly to that of **6**, while phenanthrene-extended quinone **7** shows lower reversibility because of its relatively flexible structure (Figure 4).[4c]

General Procedure for Synthesis of 1,2-Diarylacenaphthylenes (1a–f and 2)

A two-necked, round-bottomed flask equipped with a stirring bar, a rubber septum, a reflux condenser, and a N_2 balloon was charged with 1,2-dibromoacenaphthylene (**4**, 0.4 mmol), boronic acid (1.2 mmol), K_2CO_3 (3 mmol), and $Pd(PPh_3)_4$ (10 mol%). Then DME (10 mL) and H_2O (5 mL) were added through a rubber septum. The reaction mixture was stirred and refluxed for 18 h. After cooling to r.t., the mixture was poured into 2 M HCl and extracted with Et_2O (3×20 mL). The combined organic layer was washed with H_2O and brine, and dried over anhyd Na_2SO_4. After removal of the solvent, the residue was purified by column chromatography on silica gel using CH_2Cl_2–hexane as eluent to give **1**.

1,2-Diphenylacenaphthylene (1a)

Yield 85%; orange crystals; mp 159–160 °C (lit.[15] 162–163 °C). MS (EI): *m/z* (%) = 304 (100) [M^+]. ^{1}H NMR (270 MHz, $CDCl_3$): δ = 7.86 (d, *J* = 8.0 Hz, 2 H), 7.74 (d, *J* = 7.0 Hz, 2 H), 7.60 (dd, *J* = 8.0, 7.0 Hz, 2 H), 7.45 (m, 4 H), 7.30–7.39 (m, 6 H). ^{13}C NMR (67.8 MHz, $CDCl_3$): δ = 139.88, 138.02, 135.16, 129.97, 128.34, 128.27, 128.15, 127.72, 127.20, 127.01, 123.89.

1,2-Di(4-methoxyphenyl)acenaphthylene (1b)

Yield 96%; red crystals; mp 106–107 °C (lit.[3e] 122 °C). MS (EI): *m/z* (%) = 364 (100) [M^+]. ^{1}H NMR (270 MHz, $CDCl_3$): δ = 7.82 (d, *J* = 8.1 Hz, 2 H), 7.69 (d, *J* = 6.9 Hz, 2 H), 7.56 (dd, *J* = 8.1, 6.9 Hz, 2 H), 7.38 (AA′BB′, *J* = 8.9 Hz, 4 H), 6.90 (AA′BB′, *J* = 8.9 Hz, 4 H), 3.83 (s, 6 H). ^{13}C NMR (67.8 MHz, $CDCl_3$): δ = 158.56, 140.20, 136.82, 131.06, 128.23, 128.16, 127.72, 127.64, 126.85, 123.42, 113.83, 55.24. Anal. Calcd for $C_{26}H_{20}O_2$: C, 85.69; H, 5.53. Found: C, 85.54; H, 5.55.

1,2-Di(4-fluorophenyl)acenaphthylene (1c)

Yield 83%; orange crystals; mp 155–156 °C. MS (EI): *m/z* (%) = 340 [M^+]. ^{1}H NMR (270 MHz, $CDCl_3$): δ = 7.85 (dd, *J* = 8.1, 0.7 Hz, 2 H), 7.68 (dd, *J* = 6.9, 0.7 Hz, 2 H), 7.58 (dd, *J* = 8.1, 6.9 Hz, 2 H), 7.37 (m, J_{H-F} = 5.4 Hz, 4 H), 7.05 (tt, *J* = 8.8, 2.1 Hz, 4 H). ^{13}C NMR (67.8 MHz, $CDCl_3$): δ = 161.97 (d, J_{C-F} = 246.5 Hz), 139.56, 137.01, 131.48 (d, J_{C-F} = 7.8 Hz), 130.92 (d, J_{C-F} = 3.3 Hz), 128.35, 127.95, 127.77, 127.41, 123.75, 115.46 (d, J_{C-F} = 21.8 Hz). Anal. Calcd for $C_{24}H_{14}F_2$: C, 84.69; H, 4.15. Found: C, 84.34; H, 4.17.

1,2-Di(2-thienyl)acenaphthylene (1d)

Yield 94%; reddish-orange crystals; mp 140–141 °C. MS (EI): *m/z* (%) = 316 (100) [M^+]. ^{1}H NMR (270 MHz, $CDCl_3$): δ = 7.84–7.87 (m, 4 H), 7.59 (m, 2 H), 7.40 (dd, *J* = 5.1, 1.2 Hz, 2 H), 7.27 (dd, *J* = 3.6, 1.2 Hz, 2 H), 7.12 (dd, *J* = 5.1, 3.6 Hz, 2 H). ^{13}C NMR (67.8 MHz, $CDCl_3$): δ = 139.65, 136.27, 131.75, 128.24, 127.85 (2 C), 127.57, 127.24, 126.37, 124.11, 100.48. Anal. Calcd for $C_{20}H_{12}S_2$: C, 75.91; H, 3.82. Found: C, 75.81; H, 3.91.

1,2-Di(2-methylphenyl)acenaphthylene (1e)

Yield 93%; orange powder (lit.[3c] thick orange-red oil); mp 46–47 °C. MS (EI): *m/z* (%) = 332 (100) [M^+], 317 (26) [$M - CH_3]^+$, 239 (43). ^{1}H NMR (270 MHz, $CDCl_3$, mixture of two isomers): δ = 7.84 (dd, *J* = 8.0, 0.7 Hz, 2 H), 7.83 (dd, *J* = 8.1, 0.8 Hz, 2 H), 7.44–7.58 (m, 8 H), 7.09–7.30 (m, 16 H), 2.17 (s, 6 H), 2.04 (s, 6 H). ^{13}C NMR (67.8 MHz, $CDCl_3$, mixture of two isomers): δ = 140.75, 140.58, 139.52, 139.38, 136.82, 136.40, 135.03, 134.66, 130.92, 130.27, 130.25, 130.17, 128.21, 128.17, 128.08, 127.70, 127.64, 127.28, 126.91, 126.89, 125.37, 125.23, 123.76, 123.53, 20.78, 20.73.

1,2-Di(1-naphthyl)acenaphthylene (1f)

Yield 87%; orange crystals; mp 264–266 °C (lit.[7] 268–270 °C). MS (EI): *m/z* (%) = 404 (100) [M^+], 276 (18). ^{1}H NMR (270 MHz, $CDCl_3$, mixture of two isomers): δ = 8.04–8.11 (m, 4 H), 7.82–7.91 (m, 6 H), 7.69–7.76 (m, 6 H), 7.43–7.58 (m, 10 H), 7.26–7.39 (m, 8 H), 7.21–7.24 (m, 4 H), 7.08–7.14 (m, 2 H). ^{13}C NMR (67.8 MHz, $CDCl_3$, mixture of two isomers): δ = 141.17, 141.06, 139.99, 139.13, 133.58, 133.52, 133.24, 132.91, 132.82, 131.94, 128.32, 128.28, 128.20, 128.18, 128.02, 127.88, 127.81, 127.75, 127.72, 127.67, 127.22, 127.18, 126.93, 126.64, 125.56, 125.46, 125.41, 125.24, 124.99, 124.39, 124.31.

1,2-Bis(3,5-di-*tert*-butyl-4-hydroxyphenyl)acenaphthylene (2)

Yield 98%; reddish-orange crystals; mp 244–245 °C. MS (EI): *m/z* (%) = 560 (100) [M^+]. ^{1}H NMR (270 MHz, $CDCl_3$): δ = 7.80 (d, *J* = 8.1 Hz, 2 H), 7.71 (d, *J* = 6.9 Hz, 2 H), 7.56 (dd, *J* = 8.1, 6.9 Hz, 2 H), 7.23 (s, 4 H), 5.17 (s, 2 H), 1.37 (s, 36 H). ^{13}C NMR (67.8 MHz, $CDCl_3$): δ = 152.67, 140.43, 138.11, 135.64, 128.30, 128.25, 127.63, 126.71, 126.62, 126,60, 123.21, 34.36, 30.44. IR (KBr): ν = 3634 (s), 2957 (s), 1428 (s), 1399 (m), 1389 (m), 1358 (m), 1315 (m), 1234 (s), 1206 (m), 1157 (s), 1119 (m), 1034 (w), 909 (w), 889 (m), 868 (w), 823 (s), 769 (s), 651 (m) cm^{-1}. UV/Vis (cyclohexane): λ_{max} (log ε) = 458 (3.52), 356 (sh, 3.99), 340 (4.24), 328 (sh, 4.15), 294 (sh, 4.18), 280 (4.22), 254 (4.22), 238 (4.88). Anal. Calcd for $C_{40}H_{48}O_2$: C, 85.67; H, 8.63. Found: C, 85.39; H, 8.68.

1,2-Bis(3,5-di-*tert*-butyl-4-oxo-2,5-cyclohexadien-1-ylidene)-1,2-dihydroacenaphthylene (3)

A 50 mL two-necked, round-bottomed flask equipped with a stirring bar and a drying tube packed with $CaCl_2$ was charged with bisphenol **2** (115 mg, 0.2 mmol), DDQ (58 mg, 0.24 mmol), and toluene (10 mL). The reaction mixture was stirred at r.t. for 1 h. The solvent was removed under reduced pressure, and the residue was purified by column chromatography on silica gel using CH_2Cl_2–hexane = 1:5 as eluent to give **3** (91 mg, 83%).

Deep-purple crystals; mp 238–239 °C. MS (EI): *m/z* (%) = 560 (69) [M + 2 H]$^+$, 559 (43) [M + H]$^+$, 558 (100) [M^+]. ^{1}H NMR (270 MHz, $CDCl_3$): δ = 8.19 (d, *J* = 2.0 Hz, 2 H), 8.08 (d, *J* = 7.4 Hz, 2 H), 7.87 (d, *J* = 8.1 Hz, 2 H), 7.70 (dd, *J* = 8.1, 7.4 Hz, 2 H), 7.14 (d, *J* = 2.0 Hz, 2 H), 1.46 (s, 18 H), 1.21 (s, 18 H). ^{13}C NMR (67.8 MHz, $CDCl_3$): δ = 186.34, 149.71, 148.31, 147.99, 136.72, 136.46, 135.94, 132.33, 130.67, 128.39, 127.84, 127.39, 122.99, 36.20, 35.58, 29.94, 29.58. IR (KBr): ν = 3528 (m), 3443 (w), 2958 (s), 1595 (s, C=O), 1361 (m), 766 (m) cm^{-1}. UV/Vis (cyclohexane): λ_{max} (log ε) = 537 (4.04), 377 (4.60), 270 (4.14). Anal. Calcd for $C_{40}H_{46}O_2$: C, 85.98; H, 8.30. Found: C, 86.29; H, 8.22.

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(9) In agreement with literature reports,[3c,7] ^{1}H NMR spectra of **1e** and **1f** show the presence of 1:1 mixtures of rotational isomers.

(10) Boronic acid **5** was prepared by reaction of 4-bromo-2,6-di-*tert*-butylphenol with *tert*-BuLi (3 equiv)[11] and subsequently with tri(isopropoxy)borane (4 equiv). Compound **5** was obtained as a mixture with the corresponding boroxane formed by dehydration.
Compound **5**: white powder. ^{1}H NMR (270 MHz, $CDCl_3$): δ = 7.54 (s, 2 H), 5.48 (s, 1 H), 4.40 (s, 2 H), 1.47 (s 18 H). The boroxane: white powder. ^{1}H NMR (270 MHz, $CDCl_3$): δ = 8.10 (s, 6 H), 5.59 (s, 3 H), 1.53 (s, 54 H). The trimethylsilyl-protected derivative of **5** was synthesized by Satoh et al.: Satoh, Y.; Shi, C. *Synthesis* **1994**, 1146.

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(12) Crystallographic data of **3**: $C_{40}H_{46}O_2$, M = 558.80, monoclinic, $P2_1/c$, a = 21.040 (9), b = 13.717 (6), c = 24.053 (10) Å, β = 103.24 (4)°, V = 6757 (17) Å^3, Z = 8, D_c = 1.098 g cm^{-3}, 64264 reflections measured, 15373 unique (R_{int} = 0.145) used in refinement. $R1$ = 0.058 [$I > 2\sigma(I)$], wR = 0.155 (all data). T = 200 K. X-ray data have been deposited at the Cambridge Crystallographic Data Centre (CCDC-649872). Copies of the data can be obtained free of charge at www.ccdc.cam.uk/data_request/cif or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ [fax: +44 (1223)336033; e-mail: deposit@ccdc.cam.ac.uk].

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