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Convenient Synthesis of Tetra- and Hexaarylanthracenes by Means of $RuH_2(CO)(PPh_3)_3$-Catalyzed C−H Arylation of Anthraquinone with Arylboronates

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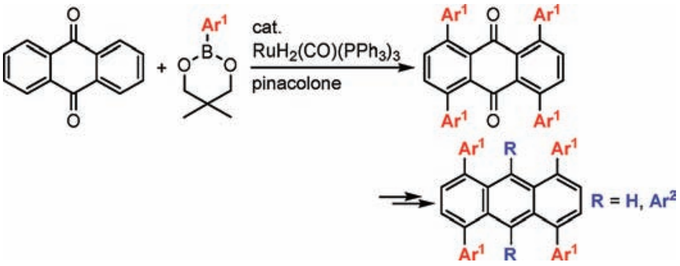
ABSTRACT



A new method for the synthesis of multiarylanthracenes was developed by means of the $RuH_2(CO)(PPh_3)_3$-catalyzed arylation of anthraquinone with arylboronates. This method consists of short and straightforward sequences starting with an easily accessible anthraquinone and is applicable to the syntheses of various multiarylanthracenes including those bearing twisted backbones.

Linearly fused polycyclic hydrocarbons, known as acenes, such as anthracenes, tetracenes, and pentacenes, have attracted much attention due to their intriguing electronic properties and potential use as organic semiconducting materials.[1] In recent years, considerable efforts have been devoted to the synthesis of new classes of functionalized acenes because the substituents may affect the electronic properties and/or the solubility.[1d,g,h] In addition, if the π-conjugated aromatic systems are highly crowded, the molecules may possess rarely observed twisted acene constructs with only singly bonded substituents.[2]

We have reported that the $RuH_2(CO)(PPh_3)_3$-catalyzed reaction of aromatic ketones with organoboronates provides orthoarylated products in high yields.[3] We envisioned that application of this C−H arylation to anthraquinone would offer convenient routes for the synthesis of multiarylated anthracenes because anthraquinone derivatives have been reported as key intermediates for the construction of substituted anthracene cores.[4]

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(1) (a) Katz, H. E.; Bao, Z.; Gilat, S. L. *Acc. Chem. Res.* **2001**, *34*, 359. (b) Dimitrakopoulos, C. D.; Malenfant, P. R. L. *Adv. Mater.* **2002**, *14*, 99. (c) Bendikov, M.; Wudl, F. *Chem. Rev.* **2004**, *104*, 4891. (d) Anthony, J. E. *Chem. Rev.* **2006**, *106*, 5028. (e) Coropceanu, V.; Cornil, J.; da Silva Filho, D. A.; Olivier, Y.; Silbey, R.; Brédas, J.-L. *Chem. Rev.* **2007**, *107*, 926. (f) Cornil, J.; Brédas, J.-L.; Zaumseil, J.; Sirringhaus, H. *Adv. Mater.* **2007**, *19*, 1791. (g) Murphy, A. R.; Fréchet, J. M. J. *Chem. Rev.* **2007**, *107*, 1066. (h) Anthony, J. E. *Angew. Chem., Int. Ed.* **2008**, *47*, 452. (i) Allard, S.; Forster, M.; Souharce, B.; Thiem, H.; Scherf, U. *Angew. Chem., Int. Ed.* **2008**, *47*, 4070.

(2) Pascal, R. A., Jr. *Chem. Rev.* **2006**, *106*, 4809.

(3) (a) Kakiuchi, F.; Kan, S.; Igi, K.; Chatani, N.; Murai, S. *J. Am. Chem. Soc.* **2003**, *125*, 1698. (b) Kakiuchi, F.; Matsuura, Y.; Kan, S.; Chatani, N. *J. Am. Chem. Soc.* **2005**, *127*, 5936.

(4) (a) Allen, C. F. H.; Bell, A. *J. Am. Chem. Soc.* **1942**, *64*, 1253. (b) Ried, W.; Donner, W.; Schlegelmilch, W. *Chem. Ber.* **1961**, *94*, 1051. (c) Anthony, J. E.; Brooks, J. S.; Eaton, D. L.; Parkin, S. R. *J. Am. Chem. Soc.* **2001**, *123*, 9482. (d) Vets, N.; Smet, M.; Dehaen, W. *Synlett* **2005**, 217.

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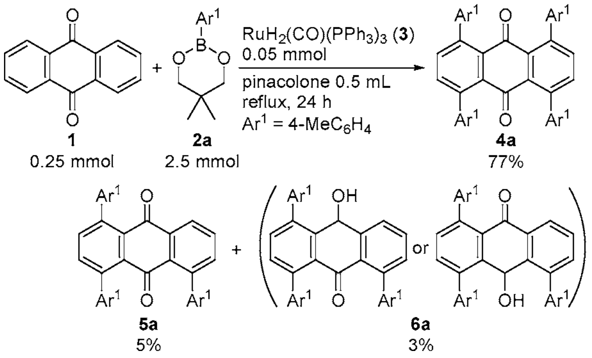
In this communication, we report the development of a new method for synthesis of multiarylanthracenes by means of the $RuH_2(CO)(PPh_3)_3$-catalyzed arylation of anthraquinone with arylboronates. This method consists of short and straightforward sequences starting with an easily accessible anthraquinone[5] and was applicable to the syntheses of various multiarylanthracenes, including those bearing twisted backbones.

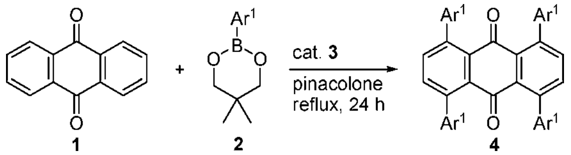
When the reaction of anthraquinone **1** with 10 equiv of *p*-tolylboronate **2a** (2.5 equiv to each ortho C−H bond) was carried out in the presence of $RuH_2(CO)(PPh_3)_3$ (**3**) as a catalyst in refluxing pinacolone, tetraarylation product **4a** was obtained in 77% isolated yield (eq 1). Triarylanthraquinone **5a** and its reduction product **6a**[6] were also isolated in 5 and 3% yields, respectively.

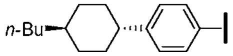


(1)

A variety of arylboronates can be used for the tetraarylation of **1** (Table 1). In the case of phenylation, the corresponding product (**4b**) was precipitated during the reaction due to the low solubility of **4b** in pinacolone (entry 1). Washing the precipitate with dichloromethane to remove the impurity provided analytically pure **4b** in 28% yield. The reaction using 3-methylphenyl- and 3,5-dimethylphenylboronates afforded tetraarylanthraquinones **4c**,**d** in 74 and 89% isolated yields, respectively (entries 2 and 3). Electronically diverse substituents (*n*-hexyl, Me_2N, OMe, and CF_3 groups) at the 4-position on the benzene ring in the arylboronates were tolerated, and the corresponding tetraarylated anthraquinones (**4e**−**h**) were isolated in 83, 33, 55, and 48% isolated yields, respectively (entries 4−7). The reaction employing a boronic acid ester (**2i**) containing a *p*-(*trans*-4-alkylcyclohexyl)phenyl moiety, found in many liquid crystals,[7] also provided the 1:4 coupling product (**4i**) in 39% yield (entry 8). Differential scanning calorimetry (DSC) analysis of **4i** showed three endothermic peaks between 150 and 280 °C during heating.

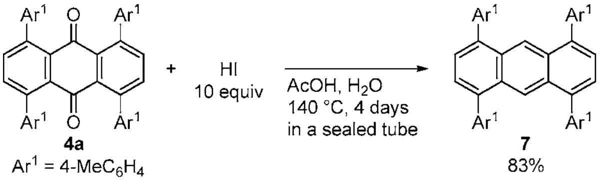
Table 1. Tetraarylation of Anthraquinone with Arylboronates[a]



entry	arylboronate	Ar	product	yield[b]
1	**2b**	Ph	**4b**	28%
2	**2c**	3-MeC_6H_4	**4c**	74%
3	**2d**	3,5-$Me_2C_6H_3$	**4d**	89%
4	**2e**	4-*n*-$HexC_6H_4$	**4e**	83%
5	**2f**	4-$Me_2NC_6H_4$	**4f**	33%
6	**2g**	4-$MeOC_6H_4$	**4g**	55%
7	**2h**	4-$F_3CC_6H_4$	**4h**	48%
8	**2i**		**4i**	39%

[a] Reaction conditions: anthraquinone (**1**) (0.25 mmol), arylboronate (**2**) (2.5 mmol), pinacolone (0.5 mL), $RuH_2(CO)(PPh_3)_3$ (**3**) (0.05 mmol), reflux, 24 h. [b] Isolated yield.

Reduction of tetra(*p*-tolyl)anthraquinone **4a** with aqueous HI and acetic acid at 140 °C in a sealed tube afforded 1,4,6,9-tetra(*p*-tolyl)anthracene (**7**) in 83% yield (eq).[5d,8] This result illustrates that the ruthenium-catalyzed tetraarylation of anthraquinone with arylboronates and the reduction with HI constitutes a convenient two-step procedure for the synthesis of tetraarylanthracenes.[9]



(2)

Conversion of **4** to hexaarylanthracenes was then examined using a reported strategy for transformation of anthraquinone moieties to diarylanthracenes (Scheme 1).[10] First, tetraphenylanthraquinone **4b** was reacted with phenyllithium in THF. Diol **8a** was obtained by arylation of both carbonyl groups

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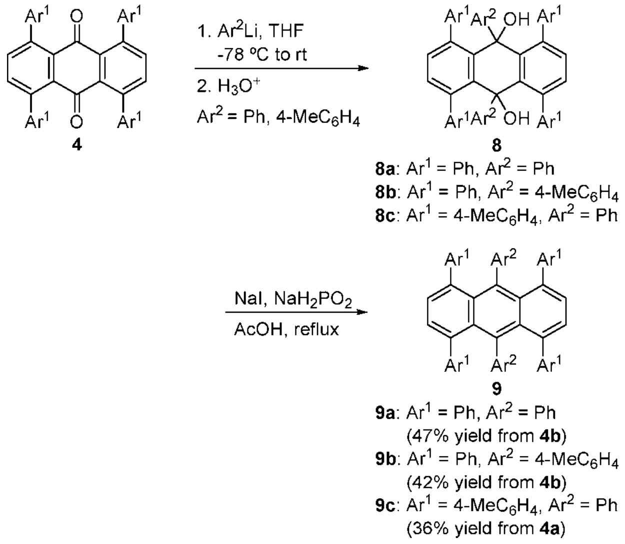
(5) For reported syntheses of highly functionalized anthracenes bearing five or more carbon substituents using Diels−Alder Reaction, see: (a) Hart, H.; Lai, C.-Y.; Nwokogu, G.; Shamouilian, S.; Teuerstein, A.; Zlotogorski, C. *J. Am. Chem. Soc.* **1980**, *102*, 6649. (b) Hart, H.; Ok, D. *J. Org. Chem.* **1986**, *51*, 979. (c) Qiao, X.; Padula, M. A.; Ho, D. M.; Vogelaar, N. J.; Schutt, C. E.; Pascal, R. A., Jr. *J. Am. Chem. Soc.* **1996**, *118*, 741. (d) Lu, J.; Zhang, J.; Shen, X.; Ho, D. M.; Pascal, R. A., Jr. *J. Am. Chem. Soc.* **2002**, *124*, 8035. (e) Rigaudy, J.; Ricard, M. M. *Tetrahedron* **1968**, *24*, 3241. For the syntheses using nucleophilic addition to carbonyl groups of oxidized anthracene frameworks, see: (f) Lepage, Y.; Pouchot, O. *Bull. Soc. Chim. Fr.* **1965**, 2342. (g) Heller, C. A.; Henry, R. A.; McLaughlin, B. A.; Bliss, D. E. *J. Chem. Eng. Data* **1974**, *19*, 214. (h) Godinez, C. E.; Zepeda, G.; Mortko, C. J.; Dang, H.; Garcia-Garibay, M. A. *J. Org. Chem.* **2004**, *69*, 1652. For the syntheses using metal-catalyzed couplings of substrates involving alkynes, see: (i) Takahashi, T.; Hara, R.; Nishihara, Y.; Kotora, M. *J. Am. Chem. Soc.* **1996**, *118*, 5154. (j) Takahashi, T.; Li, Y.; Stepnicka, P.; Kitamura, M.; Liu, Y.; Nakajima, K.; Kotora, M. *J. Am. Chem. Soc.* **2002**, *124*, 576. (k) Huang, W.; Zhou, X.; Kanno, K.-i.; Takahashi, T. *Org. Lett.* **2004**, *6*, 2429. (l) Hsieh, J.-C.; Cheng, C. H. *Chem. Commun.* **2008**, 2992. (m) Umeda, N.; Tsurugi, H.; Satoh, T.; Miura, M. *Angew. Chem., Int. Ed.* **2008**, *47*, 4019. For the syntheses using Friedel−Crafts reaction, see: (n) Marks, V.; Gottlieb, H. E.; Melman, A.; Byk, G.; Cohen, S.; Biali, S. E. *J. Org. Chem.* **2001**, *66*, 6711. (o) Yamato, T.; Sakaue, N.; Shinoda, N.; Matsuo, K. *J. Chem. Soc., Perkin Trans. 1* **1997**, 1193. For the syntheses using another approach, see: (p) Li, S.; Xiang, J.; Mei, X.; Xu, C. *Tetrahedron Lett.* **2008**, *49*, 1690. For the related palladium-catalyzed triarylation of anthrone, see: (q) Terao, Y.; Kametani, Y.; Wakui, H.; Satoh, T.; Miura, M.; Nomura, M. *Tetrahedron* **2001**, *57*, 5967–5974.

(6) Formation of **6a** was observed by ESI-MS, but the structure could not be determined by NMR analysis.

Scheme 1. Synthesis of 1,4,5,8,9,10-Hexaarylanthracenes



despite the presence of two phenyl groups in the proximity of each carbonyl group. Reduction of **8a** with NaI and NaH_2PO_2 in refluxing acetic acid afforded 1,4,5,8,9,10-hexaphenylanthracene **9a**[11] in 47% yield over two steps.

One of the features of the three-step procedure for hexaarylanthracene synthesis is that two different types of aryl groups can be introduced on the anthracene framework in a convergent manner. For example, use of *p*-tolyllithium for the arylation step led to the formation of the corresponding hexaarylanthracene (**9b**) possessing two *p*-tolyl groups at the 9- and 10-positions. Hexaarylanthracene **9c** was also obtained from tetra(*p*-tolyl)anthraquinone (**4a**) and phenyllithium. Surprisingly, however, a considerable amount of product **9c** decomposed during the isolation process under air, though structurally similar **9a** and **9b** were stable under the same conditions. Analytically pure material of **9c** was obtained in 36% yield by collecting the corresponding GPC fraction under nitrogen.

The molecular structure of hexaarylanthracene **9b** was established by X-ray diffraction analysis, and an ORTEP drawing of **9b** is illustrated in Figure 1.[12] The anthracene framework is strongly twisted, as observed for decaphenylanthracene reported by Pascal and co-workers.[5c] The end-to-end twist of **9b** is 58°, which is slightly smaller than the 63° reported for Pascal's decaphenylanthracene.[5c] These results indicate that the considerable twist of the anthracene frameworks is mainly caused by severe steric repulsion among the aryl rings at the 1-, 8-, and 9-positions or the 4-, 5-, and 10-positions. In hexaarylanthracene **9b**, the dihedral angles between the benzene rings of the anthracene moiety and the aryl groups introduced are 39−51°, which are smaller than those of decaphenylanthracene.[5c] Although compound **9b** adopts the twisted structure in the solid state, the ^{13}C NMR spectrum of **9b** in $CDCl_3$ shows only 13 peaks, indicating the conformational flexibility of **9b**, as observed for decaphenylanthracene.[5c]

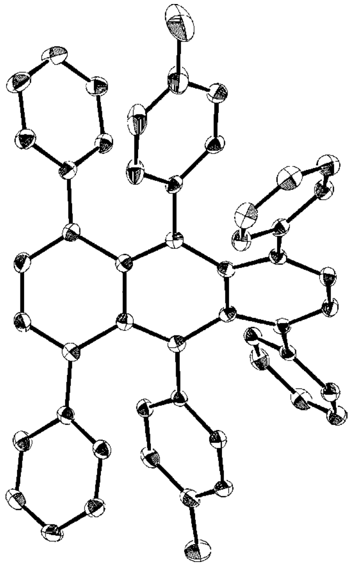


Figure 1. X-ray structure of hexaarylanthracene **9b**. Thermal ellipsoids are drawn at 50% probability level. Hydrogen atoms are omitted for clarity.

The UV absorption and fluorescence spectra of **7** and **9b** in $CHCl_3$ are shown in Figure 2. The UV absorption maximum of **7** and **9b** were observed at 397 nm (ε_{max} = 12 800) and 436 nm (ε_{max} = 26 900), respectively. The fluorescence maximum of **9b** was located at 500 nm, which

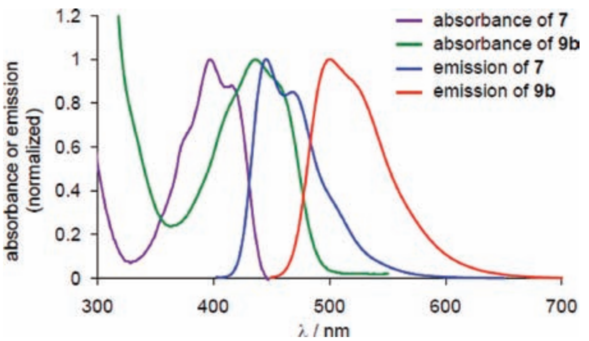


Figure 2. Normalized absorption and emission spectra of **7** and **9b**.

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(7) (a) Gray, G. W.; McDonnell, D. G. *Mol. Cryst. Liq. Cryst.* **1979**, *53*, 147. (b) Demus, D. In *Handbook of Liquid Crystals*; Demus, D., Goodby, J., Gray, G. W., Spiess, H.-W., Vill, V., Eds.; Wiley-VCH: Weinheim, Germany, 1998; Vol. 1, p 133.

(8) The reaction was carried out under the conditions modified from those reported by Pascal and co-workers.[5d] See also: Konieczny, M.; Harvey, R. G. *J. Org. Chem.* **1979**, *44*, 4813.

(9) 1,4,5,8-Tetraphenylanthracene has been the only reported 1,4,5,8-tetraarylanthracene without any other substituents: (a) Hirshberg, Y.; Haskelberg, L. *Trans. Faraday Soc.* **1943**, *39*, 45. (b) Lishan, D. G.; Hammond, G. S.; Yee, W. A. *J. Phys. Chem.* **1981**, *85*, 3435.

(10) The reactions were carried out under the conditions modified from those published by Dehaen and co-workers.[4d]

(11) Anthracene **9a** has been the only reported 1,4,5,8,9,10-tetraarylanthracene without any other substituents. See ref 5f.

was also higher than that of **7** ($\lambda_{\max} = 445$ nm). The UV and fluorescence spectra of **9b** show a significant red shift of the absortion and emission bands and broadening of the fine vibrational structure originating from the anthracene framework.[13] Quantum yields (Φ) of **7** and **9b** in $CHCl_3$ are 0.56 and 0.05, respectively.

In summary, a new straightforward method for the synthesis of tetra- and hexaarylanthracenes was developed. Anthraquinone was used as a template, and four aryl groups were introduced by direct C−H arylation employing arylboronates and the $RuH_2(CO)(PPh_3)_3$ catalyst. Reduction of the tetraarylanthraquinone product provided the corresponding tetraarylanthracene. Furthermore, the convergent synthesis of hexaarylanthracenes was achieved by the three-step procedure involving C−H arylation, addition of aryllithium reagents, and reductive aromatization. The X-ray crystallographic analysis of hexaarylanthracene **9b** revealed that the anthracene framework was highly twisted. Further application of the strategies developed here for synthesis of a variety of multiarylated acenes including ones with twisted backbones is under investigation.

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Note Added after ASAP Publication. Due to a production error equation 2 was incorrect in the version published ASAP April 8, 2009; the correct version was published April 23, 2009.

Supporting Information Available: Experimental procedures and characterization. This material is available free of charge via the Internet at http://pubs.acs.org.

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[12] Details of the crystal data and a summary of the intensity data collection parameters for **9b** are listed in Table S1 (see the Supporting Information). A suitable crystal of **9b** was mounted with cooled mineral oil to the glass fiber and transferred to the goniometer of a Rigaku Mercury CCD diffractometer with graphite-monochromated Mo Kα radiation ($\lambda = 0.71070$ Å) to $2\theta_{\max} = 50°$. The structures were solved by direct methods with SIR-97 (Altomare, A.; Burla, M. C.; Camalli, M.; Cascarano, G. L.; Giacovazzo, C.; Guagliardi, A.; Moliterni, A. G. G.; Polidori, G.; Spagna, R. *J. Appl. Crystallogr.* **1999**, *32*, 115.) and refined by full-matrix least-squares techniques against F^2 SHELXL-97. (Sheldrick, G. M. *SHELXL-97, Program for the Refinement of Crystal Structures*; University of Göttingen: Göttingen, Germany, 1997). The intensities were corrected for Lorentz and polarization effects. The non-hydrogen atoms were refined anisotropically. Hydrogen atoms were refined isotropically in the difference Fourier maps or placed using AFIX instructions. CCDC-716948 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

[13] Debad, J. D.; Lee, S. K.; Qiao, X.; Pascal, R. A., Jr.; Bard, A. J. *Acta Chem. Scand.* **1998**, *52*, 45.