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Synthesis of Functionalized Pentacenes from Isobenzofurans Derived from C−H Bond Activation

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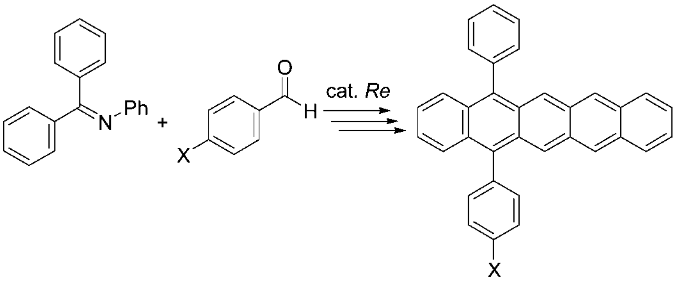
ABSTRACT



The synthesis of unsymmetric functionalized pentacenes from 1,4-anthraquinones and functionalized isobenzofurans, which were prepared by transformation via C−H bond activation, was successfully accomplished. Examples of the synthesis of pentacenes with functional groups at the 5-position are still rare. These obtained functionalized pentacenes are highly soluble in hexane, toluene, and THF.

Polyacenes are important compounds in material science.[1] Among them, pentacenes have recently received much attention because such compounds are useful as organic semiconductors, organic electron luminescent materials, organic photodiodes, and components of field effect transistors (FET) and organic solar cells.[1] To investigate the effect of substituents on the pentacene skeletons, several types of substituted pentacenes have been synthesized by various methods. These include nucleophilic addition of 2 equiv of an organometallic reagent to pentacene-6,13-dione followed by reduction,[2] reduction of pentacene-6,13-dione derivatives,[3] reduction of pentacene-5,7,12,14-tetraone derivatives,[4] Diels−Alder reaction between 2 equiv of isobenzofuran derivatives and *p*-benzoquinone followed by reduction,[5] zinc-mediated reaction of pentacene-6,13-diol with 2 equiv of thiols followed by oxidation,[6] and zirconium-mediated synthesis of polyalkylated pentacenes.[7] However, reports on the synthesis of unsymmetrical pentacenes with substituents in the 5-position are still rare.[8−11] Our strategy for the

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(2) (a) Anthony, J. E.; Eaton, D. L.; Parkin, S. R. *Org. Lett.* **2002**, *4*, 15–18. (b) Vets, N.; Smet, M.; Dehaen, W. *Synlett* **2005**, 217–222. (c) Kim, Y.; Whitten, E. J.; Swager, M. T. *J. Am. Chem. Soc.* **2005**, *127*, 12122–12130. (d) Lehnherr, D.; Murray, A. H.; McDonald, R.; Ferguson, M. J.; Tykwinski, R. R. *Chem.*−*Eur. J.* **2009**, *15*, 12580–12584.

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synthesis of unsymmetric functionalized pentacenes is as follows (Figure 1): (1) Rhenium-catalyzed synthesis of unsymmetric isobenzofurans from aromatic ketimines and aldehydes[12] and (2) Diels−Alder reaction between the formed isobenzofurans and 1,4-anthraquinone followed by reduction to give unsymmetric functionalized pentacenes.

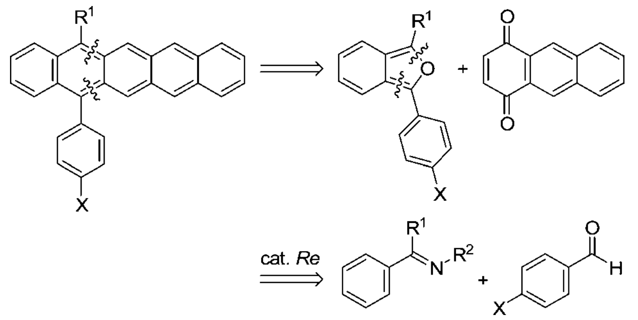


Figure 1. Strategy for the synthesis of functionalized pentacenes.

Scheme 1. Synthetic Route of Pentacene **7a**

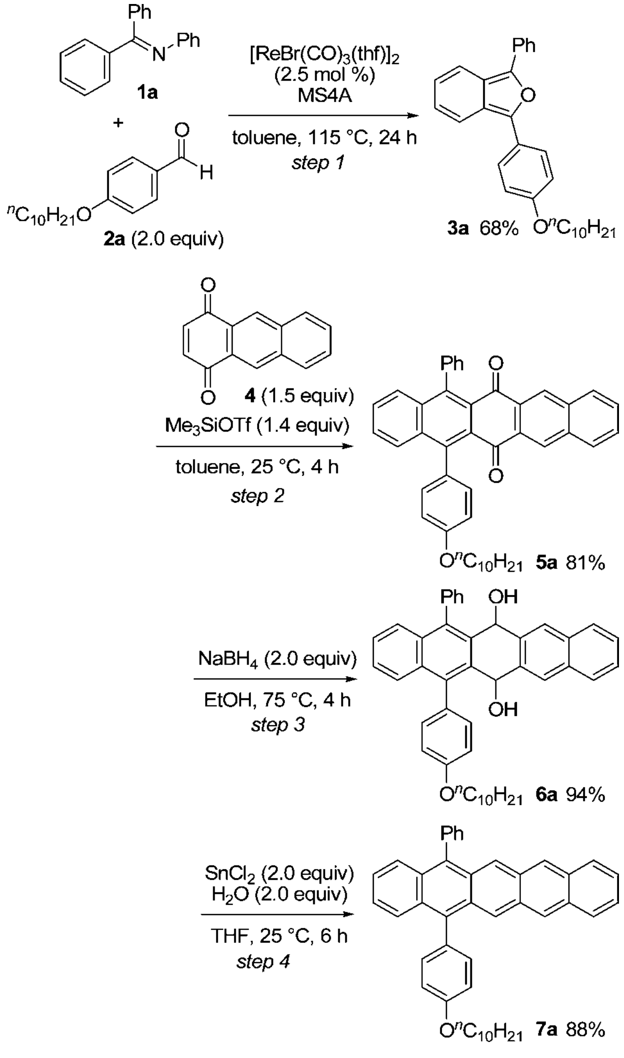
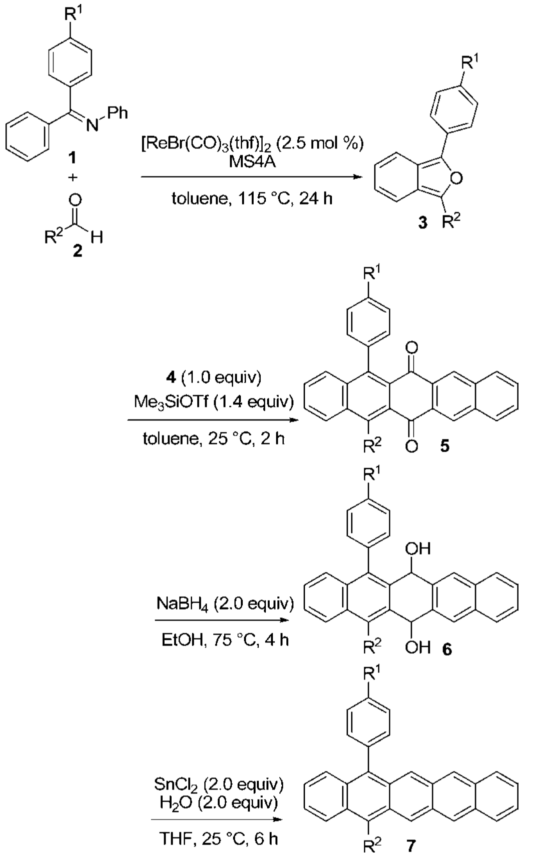
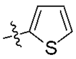
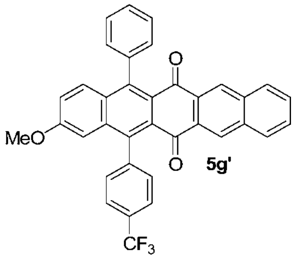


Table 1. Synthesis of Several Pentacene Derivatives **7**[a]



entry	R^1	R^2	**3** / %	**5** / %	**6** / %	**7** / %
1	H **1a**	4-(CF_3)C_6H_4 **2b**	**3b** 93	**5b** 87[b]	**6b** 99	**7b** 51[c]
2	H **1a**	4-(MeO_2C)C_6H_4 **2c**	**3c** 97	**5c** 81[b]	**6c** >99[d]	**7c** 62[e]
3	H **1a**	4-BrC_6H_4 **2d**	**3d** 59[f]	**5d** 84[b]	**6d** >99	**7d** 91[g]
4	H **1a**	4-(pinB)C_6H_4[h] **2e**	**3e** 88	**5e** 85[b]	**6e** 65	**7e** 71
5	H **1a**	 **2f**	**3f** >99	**5f** 65[i]	**6f** >99	**7f** 69
6	OMe **1b**	**2b**	**3g+3g'** >99[j] [21:79][k]	**5g** 15[l]	**6g** >99	**7g** 68[c]

[a] **2** (2.0 equiv). [b] After the reaction, **4** (0.5 equiv) was added, and the reaction mixture was stirred for an additional 2 h. [c] $SnCl_2$•$2H_2O$ (2.0 equiv) was used instead of $SnCl_2$ (2 equiv) and H_2O (2.0 equiv). [d] 2 h. After the reaction, the reaction mixture was quenched with H_2O and extracted with diethyl ether. The organic layer was concentrated in vacuo, and the residue was treated with $NaBH_4$ (2.0 equiv) and methanol at 75 °C for 2 h. [e] H_2O (4.0 equiv). [f] $[ReBr(CO)_3(thf)]_2$ (0.50 mol %), 120 h, 70%. [g] Without addition of H_2O. [h] pinB = 4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl. [i] 12 M HCl (1.4 equiv) and AcOH (0.1 M) instead of Me_3SiOTf and toluene, 2 h. [j] ^1H NMR yield. [k] The ratio between **3g** and **3g′** is given in square brackets. [l] **5g′** was obtained in 54% yield.



5g'

First, we synthesized a pentacene derivative bearing an alkoxy group (Scheme 1). Treatment of aromatic ketimine **1a** with an aromatic aldehyde having an alkoxy group at the *para*-position of the aromatic ring, **2a**, in the presence of a rhenium catalyst, $[ReBr(CO)_3(thf)]_2$, and molecular sieves in toluene at 115 °C for 24 h gave an isobenzofuran with an electron-donating group, **3a**, in 68% yield (step 1).[12] This step consists of rhenium-catalyzed C−H bond activation at the *ortho*-position of the imino group, insertion of an aldehyde into the formed rhenium−carbon bond, intramolecular nucleophilic cyclization, reductive elimination, and the elimination of aniline.[12a] By the reaction of isobenzofuran **3a** with 1,4-anthraquinone (**4**) in the presence of trimethylsilyl triflate, the Diels−Alder reaction and dehydration proceeded, and pentacenequinone **5a** was obtained in 81% yield from isobenzofuran **3a** (step 2). Reduction of pentacenequinone **5a** with sodium borohydride gave pentacenediol **6a** in 94% yield (step 3). After pentacenediol **6a** was treated with $SnCl_2$, reduction of **6a** proceeded, and a pentacene derivative having an alkoxy group, **7a**, was produced in 88% yield (step 4). In general, one problem in dealing with pentacenes is their poor solubility in many organic solvents. Pentacene **7a** is, in contrast, highly soluble in several organic solvents, including hexane, toluene, and THF.

Next, we investigated the synthesis of several pentacene derivatives following the procedure shown in Scheme 1 (Table 1). An electron-withdrawing group could be introduced into the pentacene skeleton using an aromatic aldehyde bearing a trifluoromethyl group at the *para*-position (entry 1). Pentacenes bearing methoxycarbonyl, bromo, or boryl groups, **7c**−**7e**, were synthesized using the corresponding aromatic aldehydes, **2c**−**2e** (entries 2−4). The functional groups remained intact throughout the synthesis of the pentacenes. These functional groups are useful because more complex pentacene derivatives can be prepared by transesterification[13] or cross-coupling reaction.[14] By using this method, pentacene having a heteroaromatic substituent, such as a thiophenyl group, was obtained (entry 5). Next, we investigated the synthesis of an unsymmetric difunctionalized pentacene derivative with two different functional groups (entry 6). By the reaction of the aromatic ketimine bearing a methoxy group, **1b**, with an aromatic aldehyde having a trifluoromethyl group, **2b**, in the presence of a rhenium catalyst, $[ReBr(CO)_3(thf)]_2$, a mixture of unsymmetric difunctionalized isobenzofurans **3g** and **3g′** was obtained. In this reaction, aldehyde **2b** inserted selectively into the C−H bond on the aromatic ring with the methoxy group. After converting the mixture of isobenzofurans **3g** and **3g′** to pentacenequinones **5g** and **5g′** (**5g**, 15%; **5g′**, 54%), the two isomers were separated by silica gel column chromatography. Subsequent steps were carried out as described in the equation in Table 1. As a result, a difunctional pentacene, which has both electron-withdrawing and -donating groups, **7g**, was produced. Pentacenes **7b**−**7g** are also highly soluble in toluene and THF.

In summary, we have succeeded in the synthesis of unsymmetric pentacene derivatives bearing a functional group, such as alkoxy, trifluoromethyl, methoxycarbonyl, bromo, boryl, or thiophenyl groups on the aromatic ring at the 5-position of the pentacene skeletons. The pentacenes were synthesized from functionalized isobenzofuran derivatives, which were derived by rhenium-catalyzed C−H bond transformation. These pentacenes are highly soluble in several organic solvents. We hope that this transformation will become a useful method to synthesize functionalized pentacene derivatives.

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Supporting Information Available: Typical experimental procedure, characterization data for isobenzofurans **3**, pentacenequinones **5**, pentacenediols **6**, and pentacenes **7**. This material is available free of charge via the Internet at http://pubs.acs.org.

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