ORGANIC
LETTERS

2009
Vol. 11, No. 16
3702−3705

Zirconium-Mediated Coupling Reaction for Synthesis of Substituted Thiophene-Fused Acenes

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Received May 17, 2009

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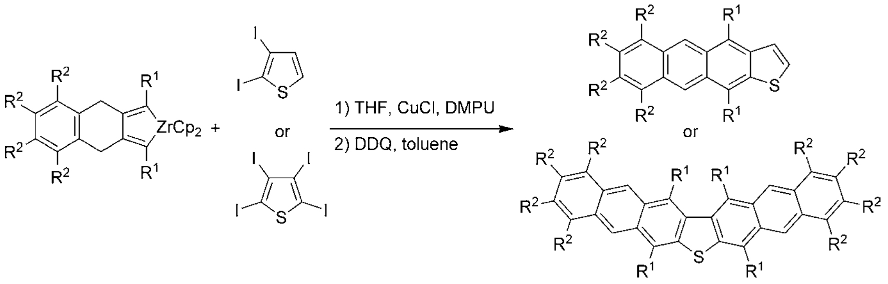
Published on July 28, 2009 on http://pubs.acs.org | doi: 10.1021/ol900903w

ABSTRACT



A novel zirconium-mediated synthesis of substituted thiophene-fused acenes is described. A variety of substituents, such as alkyl, aryl, silyl, iodo, and alkynyl groups, could be introduced to the acene skeleton by this method. Moreover, the double coupling with tetraiodothiophene gave the corresponding dianthrathiophene.

Recently, thiophene-fused higher acenes (TFHA) have been highlighted as promising candidates for organic semiconductors due to their higher durability and solubility compared to the hydrocarbon analogues without significant loss of the device performance.[1] To synthesize such a compound, the coupling reaction of metalacyclopentadienes with *o*-dihalothiophenes is a direct and efficient method. However, there was no report for preparation of TFHA using the coupling reaction.

Our group has reported two methods for the synthesis of substituted acenes based on zirconium-mediated reactions.[2,3] One is the "homologation method"[2a,b] and its modified "double homologation method",[2e] and the other is a zirconium-mediated coupling method.[3] Among them, the coupling reaction can provide a direct and simple route to highly substituted benzothiophenes[3a] and quinolines[3b] using the corresponding zirconacyclopentadienes and 1,2-dihalogenated thiophenes or pyridines, respectively. Thus, the construction of TFHA is expected by our metal-mediated

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(1) (a) Laquindanum, J. G.; Katz, H. E.; Lovinger, A. J. *J. Am. Chem. Soc.* **1998**, *120*, 664. (b) Dimitrakopoulos, C. D.; Malenfant, P. R. L. *Adv. Mater.* **2002**, *14*, 99. (c) Tang, M. L.; Okamoto, T.; Bao, Z. *J. Am. Chem. Soc.* **2006**, *128*, 16002. (d) Yuan, Q.; Mannsfeld, S. C. B.; Tang, M. L.; Toney, M. F.; Lüning, J.; Bao, Z. *J. Am. Chem. Soc.* **2008**, *130*, 3502.

(2) (a) Takahashi, T.; Kitamura, M.; Shen, B.; Nakajima, K. *J. Am. Chem. Soc.* **2000**, *122*, 12876. (b) Takahashi, T.; Li, S.; Huang, W.; Kong, F.; Nakajima, K.; Shen, B.; Ohe, T.; Kanno, K. *J. Org. Chem.* **2006**, *71*, 7967. (c) Takahashi, T.; Li, Y.; Hu, J.; Kong, F.; Nakajima, K.; Zhou, L.; Kanno, K. *Tetrahedron Lett.* **2007**, *48*, 6726. (d) Li, S.; Zhou, L.; Song, Z.; Bao, F.; Kanno, K.; Takahashi, T. *Heterocycles* **2007**, *692*, 55. (e) Li, S.; Li, Z.; Nakajima, K.; Kanno, K.; Takahashi, T. *Chem. Asian J.* **2009**, *4*, 2722. See also: (f) Stone, M. T.; Anderson, H. L. *J. Org. Chem.* **2007**, *72*, 9776.

(3) (a) Takahashi, T.; Hara, R.; Nishihara, Y.; Kotora, M. *J. Am. Chem. Soc.* **1996**, *118*, 5154. (b) Takahashi, T.; Li, Y.; Stepnicka, P.; Kitamura, M.; Liu, Y.; Nakajima, K.; Kotora, M. *J. Am. Chem. Soc.* **2002**, *124*, 576. (c) Takahashi, T.; Kashima, K.; Li, S.; Nakajima, K.; Kanno, K. *J. Am. Chem. Soc.* **2007**, *129*, 15752. (d) Seri, T.; Qu, H.; Zhou, L.; Kanno, K.; Takahashi, T. *Chem. Asian J.* **2008**, *3*, 388. (e) Zhou, L.; Nakajima, K.; Kanno, K.; Takahashi, T. *Tetrahedron Lett.* **2009**, *50*, 2722.

10.1021/ol900903w CCC: $40.75 © 2009 American Chemical Society
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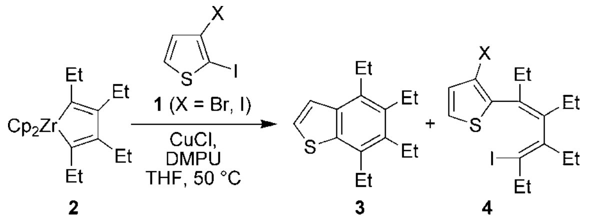
coupling methodology, although several other methods have been developed.[4−6]

In this paper, we would report a novel synthesis of variously substituted thiophene-fused higher acenes by zirconium-mediated coupling reactions.

For effective coupling with zirconacyclopentadienes, employment of 2,3-diiodothiophene was found to be essential. Table 1 showed the results of coupling of 2,3-dihalothiophene **1** and tetraethylzirconacyclopentadiene **2** under various conditions. As we reported previously, a reaction of **2** with 2-iodo-3-bromothiophene gave benzothiophene **3** but in a low yield (entry 1).[3a] We found that the major product of the reaction was a partially coupled product, iodobutadienylthiophene **4**. Although this would be converted to the desired **3**, modifications of the reaction conditions did not improve the yield of **3** (entries 2−4). When the ratio of **2** was increased, the total yield of the coupling products **3** and **4** decreased (entry 2). On the other hand, increasing the amount of **1** reduced the ratio of the desired product **3** (entry 3). Changing the solvent and reaction temperature did not improve the results (entry 4). In striking contrast to the above results with 2-iodo-3-bromothiophene, the reaction with 2,3-diiodothiophene dramatically improved the yield of **3** (entry 5). In this case, the formation of noncyclized **4** was not observed. Although the reaction of **2** with 1,2-diiodo- or 1-bromo-2-iodobenzene gave the corresponding 1,2,3,4-tetraethylnaphthalene in comparable yields, the reactivity of 2,3-diiodothiophene is significantly different from that of 2-iodo-3-bromothiophene, especially at the final cyclization coupling step.

Table 1. Coupling of Dihalothiophene **1** and Zirconacycle **2**

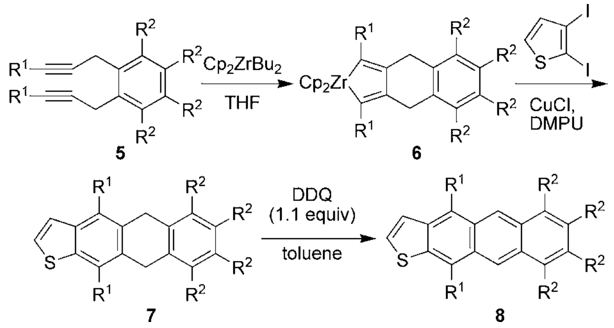


entry	1:2	X	solvent	yield of 3^a/%	yield of 4^a/%
1	1.2:1	Br	THF	22 (18)	48 (31)
2	1:4	Br	THF	15	7
3	2:1	Br	THF		61
4	1.2:1	Br	toluene	13	59
5	1.2:1	I	THF	81 (76)	0

[a] Yields were determined by GC analyses and based on the amount of the zirconacyclopentadiene. Isolated yields are shown in parentheses.

Thus, an optimized coupling reaction was applied for the synthesis of a series of anthrathiophenes as shown in Scheme 1. Diynes **5** were treated with Cp_2ZrBu_2 to form the corresponding tricyclic zirconacyclopentadienes **6**, which were coupled with 2,3-diiodothiophene in the presence of CuCl and DMPU to afford dihydroanthrathiophenes **7**. Aromatization of **7** with DDQ proceeded efficiently to afford the corresponding anthrathiophenes **8**.

Scheme 1



As summarized in Table 2, the coupling and the subsequent aromatization proceeded efficiently in all cases. When alkyl-substituted zirconacyclopentadienes were employed for the coupling reaction, the corresponding anthrathiophenes were obtained in good yields (entries 1−3). For diphenyl-substituted zirconacycle, the coupling reaction and aromatization also worked well to give diphenylated derivatives in good yields (entries 4 and 5). It is worth mentioning that silyl-substituted zirconacycle **6f** did react with 2,3-diiodothiophene, since no coupling products were obtained from the reaction of disilyl-substituted zirconacyclopentadienes with diiodobenzene under the same conditions. As mentioned above, a series of substituted anthrathiophenes were synthesized by this zirconium-mediated coupling reaction efficiently.

Table 2. Synthesis of Anthrathiophenes

entry	R^1	R^2	yield of 7^a/%	yield of 8^a/%
1	Pr	Pr	**7a**, 64 (57)	**8a**, 89 (81)
2	Bu	Bu	**7b**, 70 (55)	**8b**, 92 (80)
3	Bu	H	**7c**, 70 (43)	**8c**, 91 (84)
4	Ph	Pr	**7d**, 71 (65)	**8d**, 95 (84)
5	Ph	H	**7e**, 62 (51)	**8e**, 78 (71)
6	$SiMe_3$	Pr	**7f**, 54 (41)	**8f**, 89 (65)

[a] Yields were determined by NMR analyses and based on the amount of the zirconacyclopentadiene. Isolated yields are shown in parentheses.

Furthermore, the coupling reaction was applicable for tetraiodothiophene and the corresponding doubly coupled products were obtained (Scheme 2). The reaction of tetra-

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(4) (a) Payne, M. M.; Odom, S. A.; Parkin, S. R.; Anthony, J. E. *Org. Lett.* **2004**, *6*, 3325. (b) Lloyd, M. T.; Mayer, A. C.; Subramanian, S.; Mourey, D. A.; Herman, D. J.; Bapat, A. V.; Anthony, J. E.; Malliaras, G. G. *J. Am. Chem. Soc.* **2007**, *129*, 9144. (c) Tang, M. L.; Reichardt, A. D.; Miyaki, N.; Stoltenberg, R. M.; Bao, Z. *J. Am. Chem. Soc.* **2008**, *130*, 6064.

(5) (a) Okamoto, T.; Kudoh, K.; Wakamiya, A.; Yamaguchi, S. *Org. Lett.* **2005**, *7*, 5301. (b) Okamoto, T.; Kudoh, K.; Wakamiya, A.; Yamaguchi, S. *Chem.—Eur. J.* **2007**, *13*, 548.

(6) (a) Takimiya, K.; Kunugi, Y.; Konda, Y.; Niihara, N.; Otsubo, T. *J. Am. Chem. Soc.* **2004**, *126*, 5084. (b) Takimiya, K.; Konda, Y.; Ebata, H.; Niihara, N.; Otsubo, T. *J. Org. Chem.* **2005**, *70*, 10569. (c) Yamamoto, T.; Takimiya, K. *J. Am. Chem. Soc.* **2007**, *129*, 2224. (d) Takimiya, K.; Kunugi, Y.; Otsubo, T. *Chem. Lett.* **2007**, *36*, 578.

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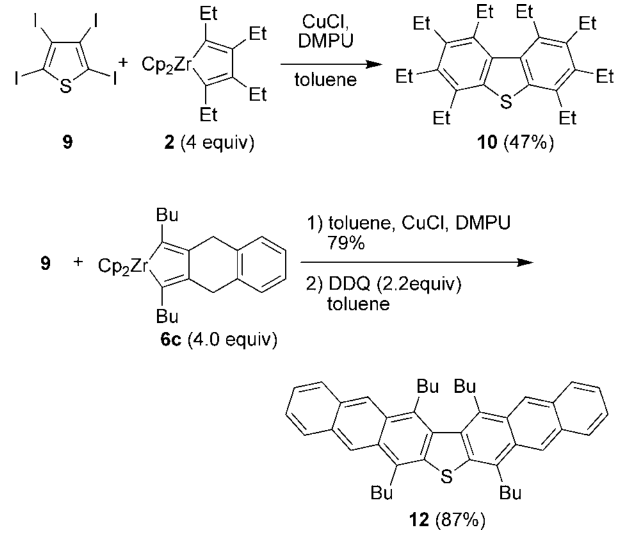
Scheme 2



ethylzirconacyclopentadiene **2** (4 equiv) with tetraiodothiophene gave the corresponding dibenzothiophene. The excess use of the zirconacycle compared to tetraiodothiophene was needed to obtain the coupling product in acceptable yield. Furthermore, the double coupling could be performed with tricyclic zirconacyclopentadiene **6c**, and the subsequent aromatization afforded the corresponding dianthrathiophene **12** in high yield. This is the first example of the formation of dianthrathiophene to the best of our knowledge. Its structure was determined by X-ray analysis as shown in Figure 1.

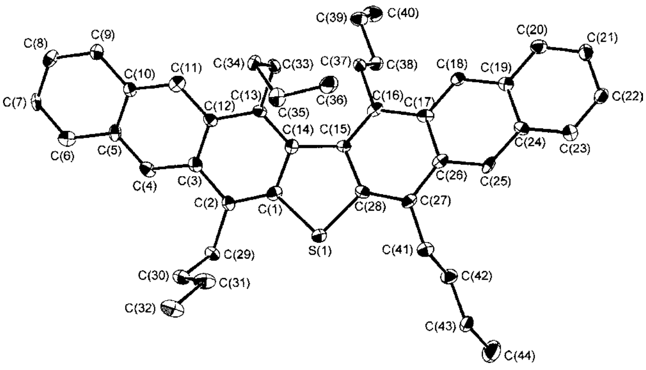
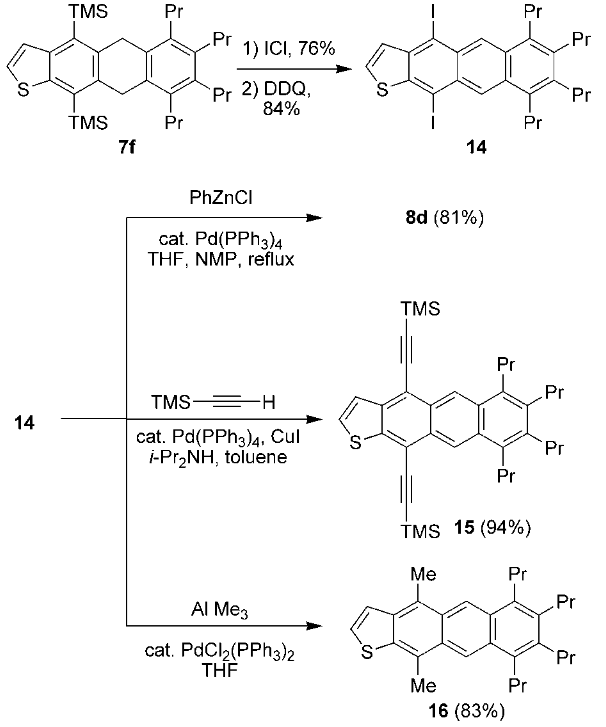


Figure 1. Perspective view of dianthrathiophene **12**.

Scheme 3



When TMS-substituted dihydroanthrathiophene **7f** was used, further derivatization was possible by utilization of well-established palladium-catalyzed cross-coupling reactions.[7] As shown in Scheme 3, trimethylsilyl groups of dihydroanthrathiophene **7f** were cleanly substituted with iodine by a reaction with ICl at −78 °C. After DDQ aromatization, thus obtained diiodoanthrathiophene **14** was subjected to cross-coupling reactions. Thus, Negishi coupling with phenylzinc chloride and Sonogashira coupling with trimethylsilylacetylene gave the corresponding coupling products **8d** and **15**, respectively, in excellent yields. Methylation of **14** with AlMe$_3$ was also possible and yielded dimethylanthrathiophene **16** in high yield. These results clearly exhibited the wide applicability of the present zirconium-mediated method for introduction of various substituents on the acene skeletons. The structure of **15** was determined by X-ray analysis as shown in Figure 2.

All of the thiophene-fused acene derivatives were highly soluble in common organic solvents, such as chloroform, ethyl acetate, hexane, and so on.

Table 3. Photophysical Properties of Anthrathiophenes[a]

compd	R^1	R^2	λ_{max}(abs) (nm)/ ε (M^{-1}cm^{-1})	λ_{max}(ems) (nm)
8a	Pr	Pr	459 (8100)	467
8b	Bu	Bu	460 (8900)	468
8c	Bu	H	450 (9400)	464
8d	Ph	Pr	463 (7600)	480
8e	Ph	H	451 (8700)	470
8f	SiMe$_3$	Pr	467 (9200)	482
14	I	Pr	473 (5500)	489
16	Me	Pr	457 (6200)	466
15	SiMe$_3$CC−	Pr	506 (10200)	525
12			506 (1100)	530

[a] Measured in CHCl$_3$ at room temperature.

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(7) *Handbood of Organopalladium Chemistry for Organic Synthesis*; Negishi, E., Meijere, A. D., Eds.; John Wiley & Sons. Inc.: New York, 2002; Vol. 1.

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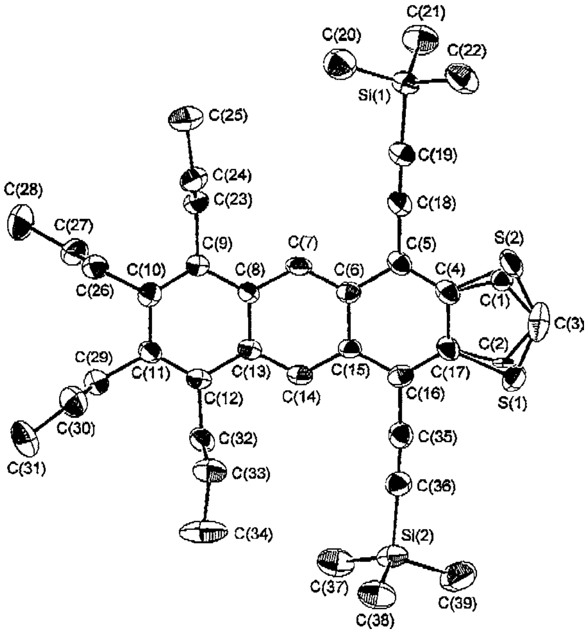

Figure 2. Perspective view of anthrathiophene **15**.

Photophysical properties of these thiophene-fused acenes were examined in chloroform as shown in Table 3, and the substituent effects were evaluated. Compared with the wavelength of the absorption maximum of dibutylanthrathiophene (**8c**), those of hexaalkyl-substituted ones were red-shifted approximately 10 nm. However, introduction of a phenyl group did not affect the outcome significantly. The absorption maxima of diphenylanthrathiophenes **8d** and **8e** were located at almost the same wavelength as those of their alkylated counterparts **8a** and **8c**, respectively. This suggests that the two phenyl groups in **8d** and **8e** do not take part in extension of π-conjugation, probably due to their preferred conformation perpendicular toward the anthrathiophene plane. In addition, substitution of heteroatoms, such as silyl (**8f**) and iodine (**14**), changes the absorption maxima slightly. In contrast, dialkynyl-substituted **15** showed the maximum at a much longer wavelength region than those of the other anthrathiophenes. In fact, the wavelength of the absorption maxmum of **15** is the same as that for dianthrathiophene **12**. This illustrates that alkynyl groups can effectively extend the π-conjugation system of the anthrathiophene moiety in contrast to the phenyl group. The substituent-dependent fluctuation of the emission maxima was almost similar to those of the absorption maxima.

In conclusion, we have developed a novel and convenient method for the synthesis of substituted anthrathiophene and dianthrathiophene derivatives mediated by zirconium. This method enables us to control various types of substitution patterns on the anthrathiophene skeletons, and alkyl, aryl, and silyl groups were introduced directly. Moreover, iodination of disilylated derivative **7f** can provide further derivatization via **14** by palladium-catalyzed cross-coupling reactions.

Supporting Information Available: Experimental procedures and spectral data for all new compounds. Crystallographic data for **12** and **15** (CIF). This material is available free of charge via the Internet at http://pubs.acs.org.

OL900903W