



Synthesis of functionalized siloles from Si-tethered diynes

Qian Luo^a, Li Gu^a, Chao Wang^a, Junhui Liu^a, Wenxiong Zhang^a, Zhenfeng Xi^{a,b,*}

^aBeijing National Laboratory for Molecular Sciences (BNLMS), Key Laboratory of Bioorganic Chemistry and Molecular Engineering of Ministry of Education, College of Chemistry, Peking University, Beijing 100871, China

^bState Key Laboratory of Organometallic Chemistry, Shanghai Institute of Organic Chemistry, Chinese Academy of Sciences, Shanghai 200032, China

ARTICLE INFO

Article history:

Received 13 January 2009

Accepted 30 January 2009

Available online 5 February 2009

Keywords:

Silole

Phenyl-bridged bis-silole

1,4-Dilithio-1,3-butadiene

1,4-Diiodo-1,3-butadiene

Si-tethered diynes

Zirconacyclopentadiene

Cleavage of Si–C bond

ABSTRACT

A new synthetic itinerary to silole from Si-tethered diynes is reported. In this protocol, the Si-tethered diyne manifests definitely the reactivity of monoyne to form the lithio silole via zirconacyclopentadiene, 1,4-diiodo-1,3-butadiene, and the corresponding dilithiodiene successively. Lithio siloles thus obtained above could be easily functionalized to give various types of silole derivatives. Complex structure like bridged bis-silole compounds could also be constructed by this process.

© 2009 Elsevier Ltd. All rights reserved.

Silacyclopentadiene, also named silole, has attracted much attention as a useful building block of π -conjugated organic materials for electronic and opto-electronic devices due to its unique electronic structure.^{1–5} A breakthrough of the synthetic method for silole was made by Tamao and Yamaguchi, in which they reduced Si-tethered diynes **1** to prepare in situ 2,5-dilithio siloles **2** or lithio benzosilole **2'** (Scheme 1).² Those lithio siloles are very important, because a wide variety of functionalized siloles can be readily synthesized by further transformation. Yet owing to the nature of the Tamao–Yamaguchi method, the substituent on diyne or the silole ring can only be the aromatic group. Recently, during our continuous research on the reactivity of 1,4-dilithio-1,3-butadiene (di-Li reagent for short),⁶ we found a facile protocol for synthesis of a new type of lithio siloles from readily available silyl di-Li reagents.^{6f} These lithio siloles are more general in terms of substitution patterns and synthetic methods, affording diversified silole derivatives. As a consecutive interest in this field, we would like to report herein a novel reaction pathway of diyne **1** to synthesize lithio silole **5** through a short route, including zirconium-mediated reductive homo-coupling of diyne **1**^{7–9} and skeletal rearrangement of silyl di-Li reagent **4**, as clarified briefly in Scheme 1. Different from the Tamao–Yamaguchi method, in this protocol diyne **1** not only exhibited the reactive property of monoyne with a comparatively broad substitution tolerance, but also can be used to construct complex framework like bridged bis-silole compounds.

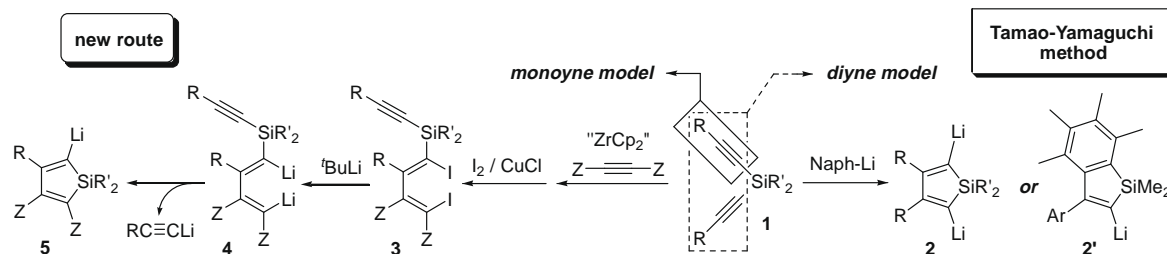
We have reported that Si-tethered diynes **1** can behave as mono triple bond to react with Negishi reagent ($\text{Cp}_2\text{Zr}^n\text{Bu}_2$), yielding zirconacyclopentadiene **6** which can change into the corresponding 1,4-diiodo-1,3-butadiene **3** by treating with CuCl and I_2 .^{8e,10} Lithiation of the di-iodide **3** with $^t\text{BuLi}$ (4 equiv) at -78°C in THF can give the di-Li reagent **4** quantitatively. The solution was then allowed to warm to room temperature and kept for 1 h before quenched with water. α -Silylated silole **7** was then obtained in excellent yield.¹¹ When D_2O was used instead to terminate the reaction of **3a**, the deuterated compound **7aD** was isolated in 90% yield with D incorporation more than 99%. On one hand, the reaction is very selective, providing **7** as the only product without observation of **7'**, which indicates that release of $\text{PhC}\equiv\text{CLi}$ is much easier than that of MeLi .^{3d,12} On the other hand, unlike Tamao–Yamaguchi method, *n*-propyl substituted silole **7b** can also be obtained in high yield from diyne **1b** smoothly, implying the electrodonating group like alkyl can also be utilized in this protocol. Indeed, the in situ generated lithio silole and alkynyl lithium were trapped at one time by adding 4-biphenylcarboxaldehyde to form the alcohol **8a** and **9**, respectively, when **3a** was used (Scheme 2).

Diyne **1a–b** could also react with another different alkyne to form unsymmetric zirconacyclopentadiene **6c–e**¹³ and mono silylated diiodobutadiene **3c–e** in sequence,¹² and the last ones can undergo similar reaction after lithiation, to give specifically the expected siloles **7c–e** as the only products in excellent yield, in spite of different types of substituent on the alkyne **1** (Scheme 3).

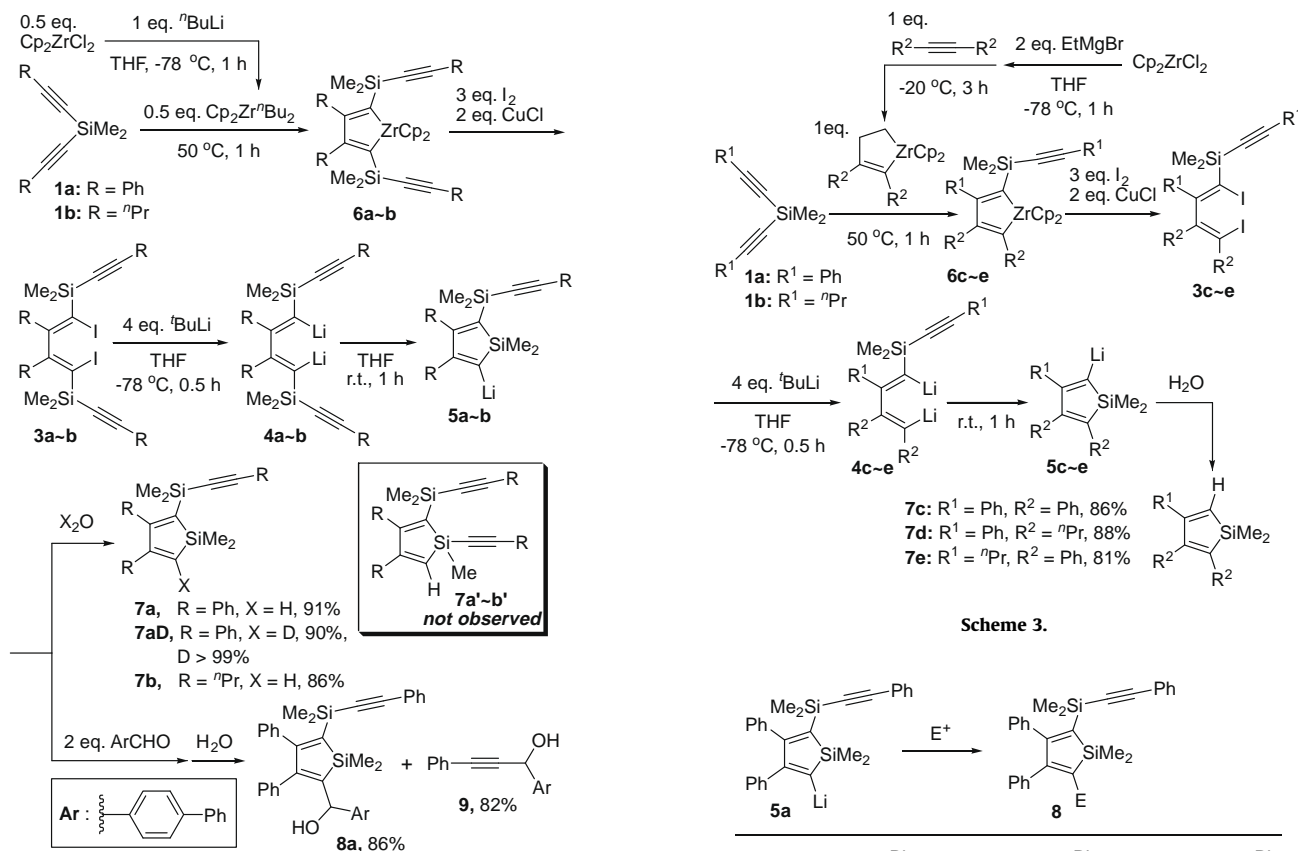
Scheme 4 demonstrated the satisfying reactivity of these readily and efficiently prepared lithio siloles **5**. For example, **5a** can be

* Corresponding author. Tel./fax: +86 10 6275 9728.

E-mail address: zfxi@pku.edu.cn (Z. Xi).



Scheme 1.

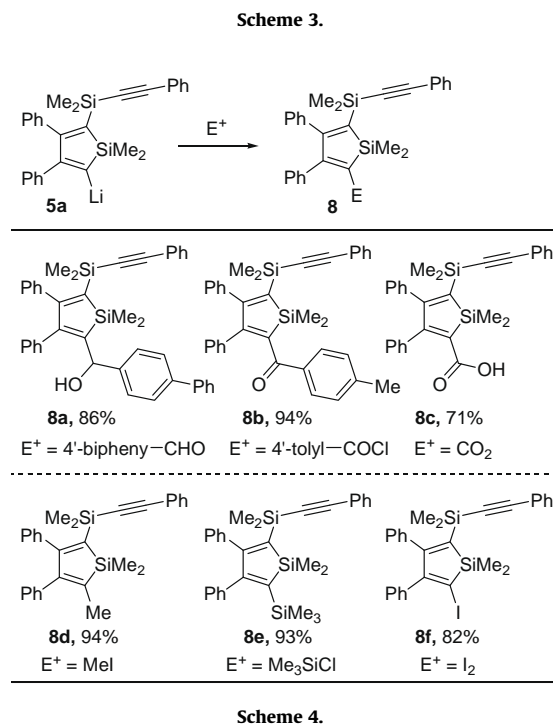


Scheme 2.

applied under different conditions to make a variety of functionalized siloles **8a-f** in one-pot with high efficiency.

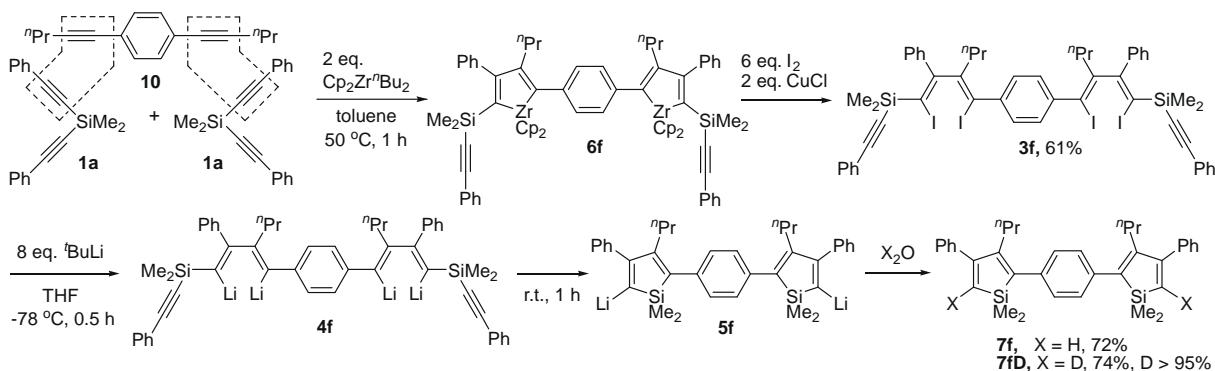
It is known that molecules with enhanced π -conjugation always lead to a set of desirable properties, such as more intense luminescence or higher carrier mobility.^{1,14} One of the promising methods to enlarge the conjugation is to join up the low-conjugated sections with various types of linkers.^{2g,15} Based on this concept, 1,4-dialkynylbenzene **10** was employed as the precursor of the linker to react with diyne **1a**, offering the tetra-iodide **3f** in 61% yield (Scheme 5). Treating this compound with similar condition as illustrated above, the acquisitive bridged bis-silole derivative **7f** was successfully gained in good yield. Stopping the reaction with D_2O also gave the relevant deuterio product **7fD**, which revealed the existence of intermediate **5f**. Compounds of this kind which contain large conjugation and complex structure are usually hard to make by ordinary method. Therefore, application of such lithio siloles as a practical synthon can be further expected.

In summary, a new itinerary to synthesize functionalized siloles from Si-tethered diynes has been discussed in this Letter. The lithio



Scheme 4.

intermediates formed in situ are useful synthons for diversified preparation of siloles. Furthermore, structurally interesting phenyl-bridged bis-silole compound has also been synthesized efficiently through this process.



Scheme 5.

Acknowledgments

This work was supported by the National Natural Science Foundation of China (20632010, 20821062, 20872005) and the Major State Basic Research Development Program (2006CB806105). The Cheung Kong Scholars Programme, Qiu Shi Science and Technologies Foundation, Dow Corning Corporation, and BASF are gratefully acknowledged.

Supplementary data

Experimental details and characterization data for all new compounds and copies of ^1H NMR and ^{13}C NMR spectra for all new compounds are available. Supplementary data associated with this article can be found, in the online version, at [doi:10.1016/j.tetlet.2009.01.152](https://doi.org/10.1016/j.tetlet.2009.01.152).

References and notes

- For recent reviews on the synthesis and property of siloles, see: (a) Yamaguchi, S.; Tamao, K. In *Silicon-containing Polymers: The Science and Technology of their Synthesis and Applications*; Jones, R. G., Ando, W., Chojnowski, J., Eds.; Kluwer Academic: Dordrecht, The Netherlands, 2000; pp 461–498; (b) Yamaguchi, S.; Tamao, K. *J. Organomet. Chem.* **2002**, *653*, 223–228; (c) Hissler, M.; Dyer, P. W.; Reau, R. *Coord. Chem. Rev.* **2003**, *244*, 1–44; (d) Yamaguchi, S.; Tamao, K. *Chem. Lett.* **2005**, 2–7; (e) Yamaguchi, S.; Xu, C. *J. Syn. Org. Chem. Jpn.* **2005**, *63*, 1115–1123; (f) Yamaguchi, S.; Xu, C.; Okamoto, T. *Pure Appl. Chem.* **2006**, *78*, 721–730; (g) Chen, J.; Cao, Y. *Macromol. Rapid Commun.* **2007**, *28*, 1714–1742.
- (a) Tamao, K.; Yamaguchi, S.; Shiro, M. *J. Am. Chem. Soc.* **1994**, *116*, 11715–11722; (b) Yamaguchi, S.; Jin, R.; Itami, Y.; Goto, T.; Tamao, K. *J. Am. Chem. Soc.* **1999**, *121*, 10420–10421; (c) Yamaguchi, S.; Endo, T.; Uchida, M.; Izumizawa, T.; Furukawa, K.; Tamao, K. *Chem. Eur. J.* **2000**, *6*, 1683–1692; (d) Yamaguchi, S.; Goto, T.; Tamao, K. *Angew. Chem., Int. Ed.* **2000**, *39*, 1695–1697; (e) Yamaguchi, S.; Xu, C.; Tamao, K. *J. Am. Chem. Soc.* **2003**, *125*, 13662–13663; (f) Xu, C.; Wakamiya, A.; Yamaguchi, S. *Org. Lett.* **2004**, *6*, 3707–3710; (g) Xu, C.; Wakayama, A.; Yamaguchi, S. *J. Am. Chem. Soc.* **2005**, *127*, 1638–1639.
- (a) Lee, J.; Yuan, Y.-Y.; Kang, Y.; Jia, W.-L.; Lu, Z. -H.; Wang, S. *Adv. Funct. Mater.* **2006**, *16*, 681–686; (b) Son, H.-J.; Han, W.-S.; Kim, H.; Kim, C.; Ko, J.; Lee, C.; Kang, S. O. *Organometallics* **2006**, *25*, 766–774; (c) Geramita, K.; McBee, J.; Shen, Y.; Radu, N.; Tilley, T. D. *Chem. Mater.* **2006**, *18*, 3261–3269; (d) Hudrlik, P. F.; Dai, D.; Hudrlik, A. M. *J. Organomet. Chem.* **2006**, *691*, 1257–1264; (e) Lee, H.; Kim, J.; Kang, Y. *Inorg. Chem. Commun.* **2007**, *10*, 731–734; (f) Ding, C.; Babu, G.; Orita, A.; Hirate, T.; Otera, J. *Synlett* **2007**, 2559–2563; (g) Booker, C.; Wang, X.; Haroun, S.; Zhou, J.; Jennings, M.; Pagenkopf, B. L.; Ding, Z. *Angew. Chem., Int. Ed.* **2008**, *47*, 7731–7735.
- (a) Liu, Y.; Chen, Z.; Chen, J.; Wang, F.; Cao, Y. *Polym. Bull.* **2007**, *59*, 31–44; (b) Heng, L.; Zhai, J.; Qin, A.; Zhang, Y.; Dong, Y.; Tang, B. Z.; Jiang, L. *Chem Phys Chem.* **2007**, *8*, 1513–1518; (c) Dong, Y.; Lam, J. W. Y.; Qin, A.; Li, Z.; Liu, J.; Sun, J.; Dong, Y.; Tang, B. Z. *Chem. Phys. Lett.* **2007**, *446*, 124–127; (d) Li, L.; Xiang, J.; Xu, C. *Org. Lett.* **2007**, *9*, 4877–4879; (e) Zhao, M.; Wang, M.; Liu, H.; Liu, D.; Zhang, G.; Zhang, D.; Zhu, D. *Langmuir* **2008**, *25*, 676–678; (f) Wang, M.; Zhang, D.; Zhang, G.; Zhu, D. *Chem. Commun.* **2008**, 4469–4471; (g) Liu, Z.; Zou, J.; Chen, J.; Huang, L.; Peng, J.; Cao, Y. *Polymer* **2008**, *49*, 1604–1610.
- (a) Ohmura, T.; Masuda, K.; Sugimoto, M. *J. Am. Chem. Soc.* **2008**, *130*, 1526–1527; (b) Ilies, L.; Tsuji, H.; Sato, Y.; Nakamura, E. *J. Am. Chem. Soc.* **2008**, *130*, 4240–4241.
- For recent applications of 1,4-dithio-1,3-dienes in organic synthesis, see: (a) Xi, Z.; Song, Q.; Chen, J.; Guan, H.; Li, P. *Angew. Chem., Int. Ed.* **2001**, *40*, 1913–1916; (b) Song, Q.; Chen, J.; Jin, X.; Xi, Z. *J. Am. Chem. Soc.* **2001**, *123*, 10419–10420; (c) Fang, H.; Li, G.; Mao, G.; Xi, Z. *Chem. Eur. J.* **2004**, *10*, 3444–3450; (d) Xi, Z. *Eur. J. Org. Chem.* **2004**, 2773–2781, and references cited therein; (e) Wang, C.; Yuan, J.; Li, G.; Wang, Z.; Zhang, S.; Xi, Z. *J. Am. Chem. Soc.* **2006**, *128*, 4564–4565; (f) Wang, C.; Luo, Q.; Sun, H.; Guo, X.; Xi, Z. *J. Am. Chem. Soc.* **2007**, *129*, 3094–3095; (g) Wang, C.; Xi, Z. *Chem. Commun.* **2007**, 5119–5133; (h) Luo, Q.; Wang, C.; Zhang, W.-X.; Xi, Z. *Chem. Commun.* **2008**, 1593–1595.
- (a) Takahashi, T.; Xi, Z.; Obora, Y.; Suzuki, N. *J. Am. Chem. Soc.* **1995**, *117*, 2665–2666; (b) Xi, Z.; Fischer, R.; Hara, R.; Sun, W.; Obora, Y.; Suzuki, N.; Nakajima, K.; Takahashi, T. *J. Am. Chem. Soc.* **1997**, *119*, 12842–12848.
- (a) Yu, T.; Deng, L.; Zhao, C.; Li, Z.; Xi, Z. *Tetrahedron Lett.* **2003**, *44*, 677–679; (b) Sun, X.; Wang, C.; Li, Z.; Zhang, S.; Xi, Z. *J. Am. Chem. Soc.* **2004**, *126*, 7172–7173; (c) Yu, T.; Sun, X.; Wang, C.; Deng, L.; Xi, Z. *Chem. Eur. J.* **2005**, *11*, 1895–1902; (d) Liu, J.; Sun, X.; Miyazaki, M.; Liu, L.; Wang, C.; Xi, Z. *J. Org. Chem.* **2007**, *72*, 3137–3140; (e) Liu, J.; Zhang, W.-X.; Guo, X.; Hou, Z.; Xi, Z. *Organometallics* **2007**, *26*, 6812–6820; (f) Liu, J.; Zhang, S.; Zhang, W.-X.; Xi, Z. *Organometallics* **2009**, *28*, 413–417.
- (a) Mao, S. S. H.; Liu, F.-Q.; Tilley, T. D. *J. Am. Chem. Soc.* **1998**, *120*, 1193–1206; (b) Pellny, P. M.; Peulecke, N.; Burlakov, V. V.; Baumann, W.; Spannenberg, A.; Rosenthal, U. *Organometallics* **2000**, *19*, 1198–1200; (c) Horacek, M.; Bazaykina, N.; Stepnicka, P.; Gyepes, R.; Cisarova, I.; Bredeau, S.; Meunier, P.; Kubista, J.; Mach, K. *J. Organomet. Chem.* **2001**, *628*, 30–38; (d) Horacek, M.; Stepnicka, P.; Gyepes, R.; Cisarova, I.; Kubista, J.; Lukesova, L.; Meunier, P.; Mach, K. *Organometallics* **2005**, *24*, 6094–6103; (e) Jin, C. K.; Yamada, T.; Sano, S.; Shiro, M.; Nagao, Y. *Tetrahedron Lett.* **2007**, *48*, 3671–3675.
- Xi, C.; Huo, S.; Affi, T. H.; Hara, R.; Takahashi, T. *Tetrahedron Lett.* **1997**, *38*, 4099–4102.
- A typical procedure for synthesis of siloles **7** from diiododiene **3**: To a 10 mL solution of 1,4-diiodo-1,3-butadiene compound **3** (1.0 mmol) in THF at -78°C was added $t\text{-BuLi}$ (4.0 mmol, 1.5 M in pentane). After this reaction mixture was stirred at -78°C for 30 min, it was warmed to room temperature and maintained for 1 h. The above reaction mixture was quenched with water and extracted with $t\text{-BuLi}$. The extract was washed with brine and dried over MgSO_4 . Solvent was then evaporated in vacuum and the residue thereafter was purified by column chromatograph using silica gel and hexane to afford title products **7**. Compound **7a**: colorless wax, 91% yield (382 mg); ^1H NMR (300 MHz, CDCl_3 , Me_4Si , 25°C): δ 0.03 (s, 6H, CH_3), 0.47 (s, 6H, CH_3), 6.29 (s, 1H, CH), 6.94–7.46 (m, 15H, CH); ^{13}C NMR (75 MHz, CDCl_3 , Me_4Si , 25°C): δ -4.00 (2CH₃), 0.82 (2CH₃), 95.10 (1 quat. C), 105.54 (1 quat. C), 123.40 (1 quat. C), 126.46 (1CH), 126.78 (1CH), 127.20 (2CH), 127.32 (2CH), 128.16 (2CH), 128.20 (2CH), 128.35 (1CH), 128.60 (2CH), 131.80 (2CH), 135.95 (1CH), 139.20 (1 quat. C), 140.91 (1 quat. C), 142.32 (1 quat. C), 161.78 (1 quat. C), 168.14 (1 quat. C); HRMS calcd for $\text{C}_{28}\text{H}_{28}\text{Si}_2$: 420.1730, found 420.1721. For more details, see Supplementary data.
- Wang, Z.; Fang, H.; Xi, Z. *Tetrahedron Lett.* **2005**, *46*, 499–501.
- (a) Xi, Z.; Hara, R.; Takahashi, T. *J. Org. Chem.* **1995**, *60*, 4444–4448; (b) Hara, R.; Xi, Z.; Takahashi, T. *Chem. Lett.* **1996**, 1003–1004.
- For reviews on ladder π -conjugated molecules: (a) Martin, R. E.; Diederich, F. *Angew. Chem., Int. Ed.* **1999**, *38*, 1350–1377; (b) Scherf, U. *J. Mater. Chem.* **1999**, *9*, 1853–1864; (c) Watson, M. D.; Fechtenkötter, A.; Müllen, K. *Chem. Rev.* **2001**, *101*, 1267–1300; (d) Katz, H. E.; Bao, Z.; Gilat, S. L. *Acc. Chem. Res.* **2001**, *34*, 359–369; (e) Bendikov, M.; Wudl, F.; Perepichka, D. F. *Chem. Rev.* **2004**, *104*, 4891–4946.
- (a) Boydston, A. J.; Yin, Y.; Pagenkopf, B. L. *J. Am. Chem. Soc.* **2004**, *126*, 10350–10354; (b) Matsuda, T.; Kadowaki, S.; Murakami, M. *Chem. Commun.* **2007**, 2627–2629.