Tetrahedron Letters 51 (2010) 4526–4529

Contents lists available at ScienceDirect

Tetrahedron Letters

journal homepage: www.elsevier.com/locate/tetlet

A selective and direct synthesis of 2-bromo-4-alkylthiophenes: Convenient and straightforward approaches for the synthesis of head-to-tail (HT) and tail-to-tail (TT) dihexyl-2,2′-bithiophenes

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ARTICLE INFO

Article history:
Received 21 April 2010
Revised 12 June 2010
Accepted 21 June 2010
Available online 25 June 2010

Keywords:
Alkylthiophenes
Bromination
Grignard reagents
2,2′-Bithiophenes
Dihexylbithiophenes
HH- and TT-cross-couplings
Kumada and Suzuki cross-couplings

ABSTRACT

A straightforward method for the synthesis of 2-bromo-4-alkylthiophenes was developed, and the desired products were obtained in the highest chemical yields (>90%) reported to date. 2-Bromo-4-alkylthiophenes were synthesized by regioselective lithiating of 3-alkylthiophenes with *n*-BuLi and quenching with bromine at −78 °C. Moreover, a simple and efficient protocol for the synthesis of dihexyl-2,2′-bithiophenes was developed by employing 2-bromo-4-hexylthiophene instead of the commonly used monomer, 2-bromo-3-hexylthiophene. Kumada and Suzuki cross-coupling reactions were conducted to synthesize the desired products as head-to-tail (HT) and tail-to-tail (TT) regioisomers in high yields and excellent selectivity.

Oligo- and polythiophenes have received substantial attention as potential materials in photovoltaic and electroluminescence devices.[1] Poly(3-alkylthiophenes) (P3ATs) are one of the most extensively studied conductive polymers of the past decade due to their high solubility and interesting electrochemical and physical properties.[2] Recently, oligo- and poly-3ATs with dramatically improved properties have been produced by a regioregular synthesis.[3,4] The substrates used in the preparation of oligo- and poly-3ATs are neither centrosymmetric nor do they possess a symmetry axis; thus, three possible isomeric diads can be formed from the coupling of 3-alkylthiophenes. As a result, four types of spectroscopically distinct nonequivalent triads are detected in the NMR spectra.[4–7] However, head-to-head couplings are unfavorable due to steric repulsion between the alkyl chains and the lone pairs of electrons on the adjacent sulfur atoms.[4,6,7] Thus, an efficient synthesis of alkylthiophenes would provide access to oligo- and polythiophenes, which may lead to the development of new devices and applications of polymer-based materials.

Kumada[4,6,8,9] and Suzuki[10] cross-coupling methods have been used extensively for the synthesis of head-to-tail and tail-to-tail oligo- and poly-ATs. Alternatively, cryogenic lithiation of 2-halo-3-alkylthiophenes and the subsequent treatment with organotin or organoboron electrophiles is an efficient method for generating monomers for the regiospecific synthesis of oligo- and poly-ATs.[4,11,12] Thus, halothiophenes are one of the most important structures for the homocoupling of thiophenes. Upon treatment with a stoichiometric amount of *N*-bromosuccinimide, 3-alkylthiophenes quantitatively transformed into 2-bromo-3-alkylthiophenes.[13,14] The reaction is complete within a few minutes at ambient or slightly elevated temperatures, and overbromination typically leads to the corresponding 2,5-dibromo-3-alkylthiophenes.[14] Although brominating the α-position of 3-alkylthiophenes has been investigated extensively, few methods allow for the selective bromination of the 5th position of 3-alkylthiophenes.[6,15]

Reinecke et al. have investigated the bromination of 3-methylthiophene by reacting the substrate with *n*-BuLi and quenching with bromine.[15b] An inseparable mixture of products was obtained, and the desired product (2-bromo-4-methylthiophene) was difficult to isolate in reasonable yield and purity.[15b] Interestingly, de Meijere et al. have also recently reported on the synthesis of 2-bromo-4-methylthiophene in 55% yield by lithiating 3-methylthiophene with

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doi:10.1016/j.tetlet.2010.06.100

n-BuLi followed by treating the resulting 2-lithio-4-methyl derivative with *N*,*N*,*N*′,*N*′-tetramethyl-1,2-ethylenediamine (TMEDA) and quenching with CBr$_4$.[15d]

As shown in Scheme 1, McCullough and co-workers synthesized 2-bromo-4-butylthiophene (**5a**) in four distinct steps starting from 3-butylthiophene (**1a**).[6] To generate 2-bromo-4-butylthiophene, the TMS-blocking group was removed from 2-trimethylsilyl-3-butyl-5-bromothiophene (**4**) and the desired product **5a** was obtained in 73% yield. Moreover, the synthesis of 2-bromo-4-dodecylthiophene has been achieved by lithiating 3-dodecylthiophene and reacting the lithiated intermediate with carbon tetrabromide (CBr$_4$).[6] The crude product mixture consisted of 3-dodecylthiophene and both isomers of the desired product in a 9:1 ratio. However, due to side reactions and poor recovery, the overall yield of 2-bromo-4-dodecylthiophene was very low (23%).

Recently, Luscombe et al. synthesized 2-bromo-4-hexylthiophene (**5b**) by lithiating 3-hexylthiophene (**1b**) with *n*-BuLi followed by treating the lithiated intermediate with TMEDA and CBr$_4$ (Scheme 2).[15e] However, after fractional distillation, the desired product was obtained in only ~11% yield.

Due to the limitations in the aforementioned synthesis, we developed an efficient and straightforward method for the synthesis of 2-bromo-4-alkylthiophenes, and obtained the highest chemical yields reported to date. Moreover, Kumada and Suzuki cross-coupling of 2-bromo-4-hexylthiophene was conducted to synthesize dihexyl-2,2′-bithiophenes in high chemical yields and excellent selectivity.

Lithiation of 3-alkylthiophenes occurs predominantly at the carbon-γ to the alkyl chain, however, sterically hindered alkyl substituents increase the selectivity of lithiation.[6,11,12,15e] Thus, 3-alkylthiophenes (**1a**–**c**) were lithiated with *n*-BuLi at −78 °C and subsequently quenched with bromine at the same temperature. 2-Bromo-4-alkylthiophenes (**5a**–**c**) were produced, along with trace amounts of 2,5-dibromo-3-alkylthiophenes (**6a**–**c**) (Scheme 3). After the addition of bromine, the color of the reaction mixture changed within only few minutes, indicating the reaction was completed. A slight excess of bromine ensured complete conversion to the desired product.

When bromine was added to the reaction mixture in one portion at −78 °C or at elevated temperatures, the desired products **5a**–**c** were formed in low to moderate yields (43–67%) due to scrambling at the α-carbon adjacent to the alkyl groups of **1a**–**c** by hydrogen–bromide exchange.[12–14] Significant amounts of the starting material **1**, as well as 2-bromo- and 2,5-dibromo-3-alkylthiophenes (**2** and **6**, respectively), were detected and fully characterized. Very slow addition of Br$_2$ (as a solution in THF) was necessary to achieve satisfactory results. Moreover, after the complete addition of bromine, when water and/or aqueous NaOH was added to the reaction mixture, at ambient or even lower temperature, the desired products **5a**–**c** were obtained in low yields as a mixture of isomeric products. To achieve selective formation of the desired products, the reaction must be ended at −78 °C. It was realized that adding a few drops of an aqueous methanolic solution of sodium thiosulfate at −78 °C was found to be a suitable method for ending the reaction. These modifications provided 2-bromo-4-alkylthiophenes (**5a**–**c**) in high yields (>90%). Several attempts to isolate the desired products **5a**–**c** by fractional distillation failed to afford good yields; however, the desired products could be obtained in excellent purity with high yields by careful silica gel flash chromatography.

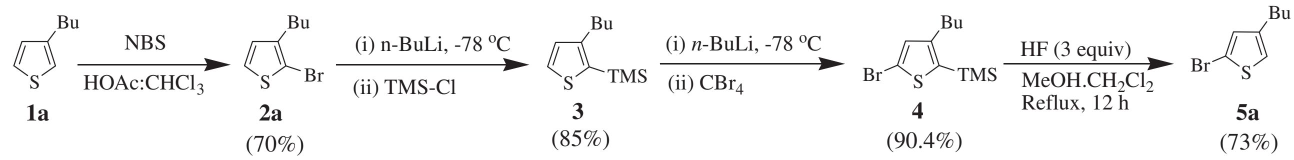
The structure of 2-bromo-4-alkylthiophenes (**5a**–**c**) was characterized and confirmed by each of ^{1}H and ^{13}C NMR spectroscopy (see Supplementary data). The ^{1}H and ^{13}C NMR spectra of the resulting 2-bromo-4-alkylthiophenes were fully consistent with the expected structures.

Kumada cross-coupling of thienylmagnesium bromides and bromothiophenes is a useful method for the homologation of thiophenes and the synthesis of oligo- and polythiophenes.[4,6,8,9] Thus, we attempted the biaryl coupling of 3-hexylthiophene according to the Kumada cross-coupling procedure. 2-Bromo-4-hexylthiophene (**5b**) reacted readily with magnesium, resulting in the exclusive formation of 4-hexyl-2-thienylmagnesium bromide (**7**) (Scheme 4). To verify the formation of the Grignard reagent **7** in a good yield, **5b** was reacted with magnesium and quenched with 2 M HCl. Nearly quantitative conversion to 3-hexylthiophene (**1b**) was observed, along with a negligible amount of 2-bromo-4-hexylthiophene (**5b**), as shown by GC–MS, ^{1}H, and ^{13}C NMR analyses.

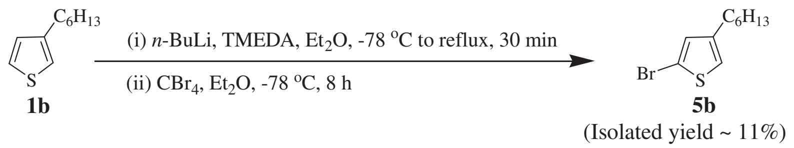
Kumada cross-coupling of the intermediate **7** with **2b** and/or **5b** in the presence of catalytic amounts of Ni(dppp)Cl$_2$ yielded exclusively the corresponding coupled products 3,4′-dihexyl-2,2′-bithiophene (**8**) and 4,4′-dihexyl-2,2′-bithiophene (**9**), in high yields (Scheme 4). The coupled product **8** was also readily prepared in high yield (92%) via Kumada cross-coupling of 3-hexyl-2-thienylmagnesium bromide (**10**)[5h,13,15] and **5b** in the presence of catalytic amounts of Ni(dppp)Cl$_2$ (Scheme 4). It is worth to mention that bithiophenes **8** and **9** have not been synthesized by this synthetic pathway; however, 3,4′-dihexyl-2,2′-bithiophene (**8**) was previously prepared in 75% yield by a metal-free oxidative biaryl-coupling reaction of 3-hexylthiophene (**1b**) and a recyclable hypervalent iodine (III) reagent in the presence of TMSBr.[16] Moreover, 4,4′-dihexyl-2,2′-bithiophene (**9**) was previously prepared in 52% yield by reacting 3-hexylthiophene with *n*-BuLi at −78 °C and treating the lithiated intermediate with CuCl$_2$.[11a]

The reactivity of 2-bromo-4-hexylthiophene (**5b**) in the Kumada cross-coupling reaction was satisfactory. Compared to 2-bromo-3-hexylthiophene (**2b**), the bromine in 2-bromo-4-hexylthiophene (**5b**) was more reactive and the corresponding Grignard reagent was formed rapidly. However, the oxidative addition of Ni(cod)$_2$ (cod = 1,5-cyclooctadiene) to 2,5-dibromo-3-alkylthiophenes occurs preferentially at the fifth position of the thiophene ring due to the less amount of steric hindrance relative to the second position.[2f,4,17] Similar to the results obtained by Grignard Metathesis Method (GRIM) for the synthesis of HH and TT-poly-ATs, the lack of steric congestion facilitates the formation of an intermediate between the bromine atom in 2-bromo-4-hexylthiophene (**5b**) and Ni(dppp)Cl$_2$, which leads to TT and HT couplings.[4,6,7]

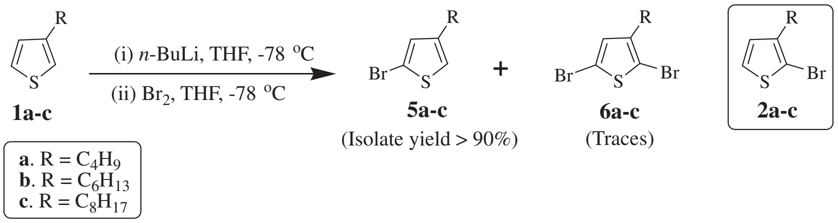
The lithiation of 2-bromo-4-hexylthiophene (**5b**) with *n*-BuLi at −78 °C and the subsequent reaction with triisopropylborate and pinacol afforded 2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolane)-4-hexylthiophene (**11**) in excellent yield (95%, Scheme 5). However, boronic ester **11** has been previously synthesized in 89% yield by reacting 3-hexylthiophene (**1b**) with *n*-BuLi at −78 °C and subsequently treating the lithiated intermediate with 2-isopropoxy-4,4,5,5-tetramethyl-1,3,2-dioxaborolane.[11]



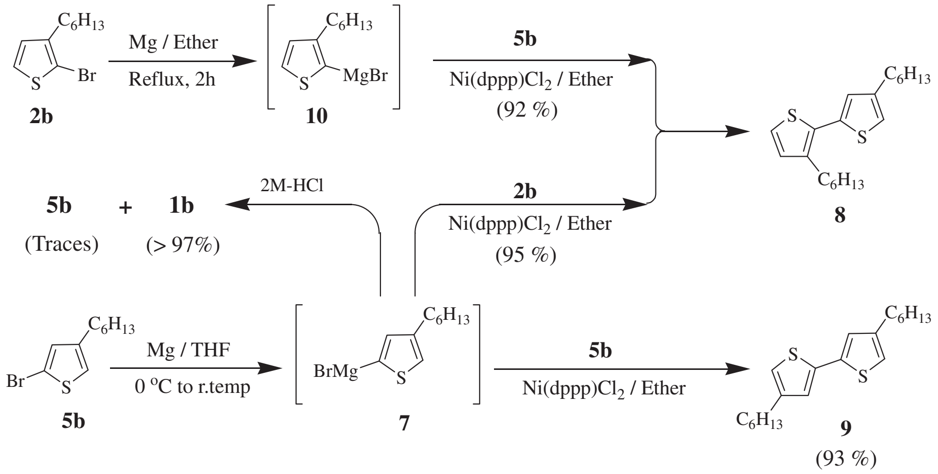
Scheme 1. Synthesis of 2-bromo-4-butylthiophene in four distinct steps, starting from 3-butylthiophene, with an overall yield of 73%.[6]



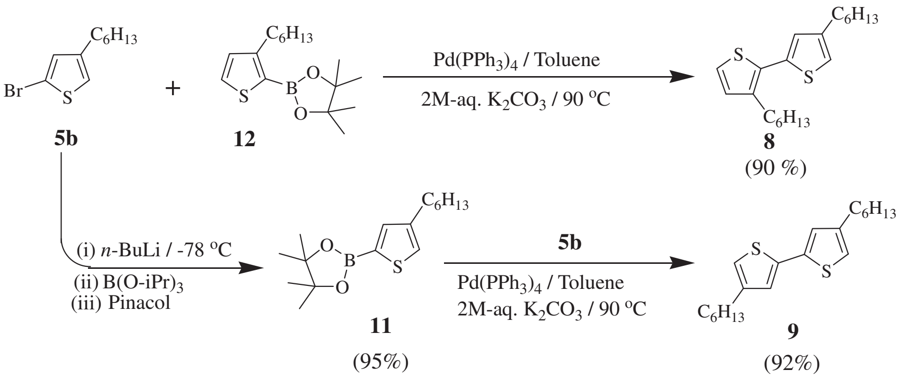
Scheme 2. Synthesis of 2-bromo-4-hexylthiophene (**5b**) by lithiating 3-hexylthiophene (**1b**) with *n*-BuLi followed by treating the lithiated intermediate with *N*,*N*,*N*′,*N*′-tetramethyl-1,2-ethylenediamine (TMEDA) and CBr_4.[15e]



Scheme 3. Synthesis of 2-bromo-4-alkylthiophenes (**5a–c**) by lithiating 3-alkylthiophenes (**1a–c**) with *n*-BuLi at −78 °C followed by quenching with bromine at the same temperature.



Scheme 4. Synthesis of 3,4′-dihexyl-2,2′-bithiophene (**8**) and 4,4′-dihexyl-2,2′-bithiophene (**9**) via Kumada cross-coupling method.



Scheme 5. Synthesis of 3,4′-dihexyl-2,2′-bithiophene (**8**) and 4,4′-dihexyl-2,2′-bithiophene (**9**) via Palladium-catalyzed Suzuki cross-coupling method.

Palladium-catalyzed Suzuki cross-coupling of boronic ester **11** with 2-bromo-4-hexylthiophene (**5b**) in the presence of $Pd(PPh_3)_4$ preceded efficiently and afforded 4,4′-dihexyl-2,2′-bithiophene (**9**) in 92% yield as the tail-to-tail regioisomer. Interestingly, Suzuki cross-coupling of 2-bromo-4-hexylthiophene (**5b**) with 2-(4,4,5,5-tetramethyl-1,3,2-dioxaborolane)-3-hexylthiophene (**12**) in the presence of $Pd(PPh_3)_4$ afforded 3,4′-dihexyl-2,2′-bithiophene (**8**) in excellent head-to-tail regioselectivity and high yield (90%).

It is worth to mention that 3,4′-dihexyl-2,2′-bithiophene (**8**) has been previously prepared in 62% yield by the Suzuki cross-coupling of **11** and **2b** in the presence of $Pd(PPh_3)_4$.[11a] Moreover, bithiophene **8** has also been synthesized in 70% yield by reacting

3-hexyl-2-iodothiophene with sodium 4-hexylthiophene-2-boronate in the presence of Pd(PPh_3)$_4$.[18] The aforementioned results indicated that lithiation of the 2nd position of 2-bromo-4-hexylthiophene (**5b**) becomes more regioselective than lithiation of the 5th position compared to lithiation of 3-hexylthiophene (**1b**).

In conclusion, we have developed a selective method for the synthesis of 2-bromo-4-alkylthiophenes (**5a**–**c**) in high yields (>90%). The present method is superior to the previously reported methods for their synthesis.[6,15e] Dihexyl-2,2′-bithophenes **8** and **9** were readily synthesized via Kumada and Suzuki cross-coupling methods and the yields of the desired products, in most cases, were superior to those reported in the literatures. We believe that the proposed synthetic method can be used for the step-wise construction of oligo- and polythiophenes with well-defined structures. To investigate the optical and electrical properties of oligo- and poly-ATs, further syntheses are currently being developed.

Acknowledgments

This work was supported by the Program for Integrated Molecular Systems (PIMS) and the World Class University (WCU) Program, Korea (Project No. R31-20008-000-10026-0). (RISE), Korea. The author (A.A.E.-S.) would like to thank the Korean Brain Pool Program supported by the Korean Federation of Science and Technology Societies (KOFST).

Supplementary data

Supplementary data (experimental details and the spectral data for the synthesized 2-bromo-4-alkylthiophenes) associated with this article can be found, in the online version, at doi:10.1016/j.tetlet.2010.06.100.

References and notes

1. (a) Fichou, D. *J. Mater. Chem.* **2000**, *10*, 571–588; (b) Otsubo, T.; Aso, Y.; Takimiya, K. *J. Mater. Chem.* **2002**, *12*, 2565–2575; (c) Barbarella, G. *Electron. Opt. Prop. Conjug. Mol. Syst. Conden. Phases* **2003**, 79–97; (d) Hotta, S.; Ichino, Y.; Yoshida, Y. *Electron. Opt. Prop. Conjug. Mol. Syst. Conden. Phases* **2003**, 615–635; (e) Hotta, S. *Trans. Mater. Res. Soc. Jpn.* **2004**, *29*, 985–990; (f) James, D. K.; Tour, J. M. *Top. Curr. Chem.* **2005**, *257*, 33–62; (g) Otsubo, T.; Aso, Y.; Takimiya, K. *Pure Appl. Chem.* **2005**, *77*, 2003–2010; (h) Perepichka, I. F.; Perepichka, D. F.; Meng, H.; Wudl, F. *Adv. Mater.* **2005**, *17*, 2281–2305; (i) Locklin, J.; Roberts, M.; Mannsfeld, S.; Bao, Z. *Polym. Rev.* **2006**, *46*, 79–101; (j) Murphy, A. R.; Frechet, J. M. *J. Chem. Rev.* **2007**, *107*, 1066–1096; (k) Osaka, I.; Mccullough, R. D. *Acc. Chem. Res.* **2008**, *41*, 1202–1214; (l) Briseno, A. L.; Holcombe, T. W.; Boukai, A. I.; Garnett, E. C.; Shelton, S. W.; Fréchet, J. J. M.; Yang, P. *Nano Lett.* **2010**, *10*, 334–340.
2. (a) Kowalik, J.; Tolbert, L. M.; Narayan, S.; Abhiraman, A. S. *Macromolecules* **2001**, *34*, 5471–5479; (b) Nguyen, L. H.; Hoppe, H.; Erb, T.; Günes, S.; Gobsch, G.; Sariciftci, N. S. *Adv. Funct. Mater.* **2007**, *17*, 1071–1078; (c) Singh, R.; Kumar, J.; Singh, R. K.; Rastogi, R. C.; Kumar, V. *New J. Phys.* **2007**, *9*, 40–61; (d) Günes, S.; Neugebauer, H.; Sariciftci, N. S. *Chem. Rev.* **2007**, *107*, 1324–1338; (e) Günes, S.; Baran, D.; Günbas, G.; Özyurt, F.; Fuchsbauer, A.; Sariciftci, N. S.; Toppare, L. *Sol. Energy Mater. Sol. Cells* **2008**, *92*, 1162–1169; (f) Wu, P.-T.; Xin, H.; Kim, F. S.; Ren, G.; Jenekhe, S. A. *Macromolecules* **2009**, *42*, 8817–8826; (g) Wu, C.-G.; Lai, C.-Y.; Hsiao, N.-L. *Eur. Polym. J.* **2009**, *45*, 879–887; (h) Lanzi, M.; Paganin, L. *React. Funct. Polym.* **2010**, *70*, 346–360.
3. (a) Pal, S.; Nandi, A. K. *Macromolecules* **2003**, *36*, 8426–8432; (b) Al-Ibrahim, M.; Roth, H.-K.; Schroedner, M.; Konkin, A.; Zhokhavets, U.; Gobsch, G.; Scharff, P.; Sensfuss, S. *Org. Electron.* **2005**, *6*, 65–77; (c) Vandeleene, S.; Bergh, K. V.; Verbiest, T.; Koeckelberghs, G. *Macromolecules* **2008**, *41*, 5123–5131; (d) Arosio, P.; Moreno, M.; Famulari, A.; Raos, G.; Catellani, M.; Meille, S. V. *Chem. Mater.* **2009**, *21*, 78–87; (e) Cai, W.; Gong, X.; Cao, Y. *Sol. Energy Mat. Sol. Cells* **2010**, *94*, 114–127.
4. (a) Trznadel, M.; Porn, A.; Zagorska, M.; Chrzaszcz, R.; Pielichowski, J. *Macromolecules* **1998**, *31*, 5051–5058; (b) Chou, Y.-M.; Chen, W.-H.; Liang, C.-C. *J. Mol. Struct. Theor. Chem.* **2009**, *894*, 117–120.
5. (a) Sato, M.; Morii, H. *Macromolecules* **1991**, *24*, 1196–1200; (b) Sato, M.; Morii, H. *Polym. Commun.* **1991**, *32*, 436–438; (c) ZagSrska, M.; Kulszewicz-Bajer, I. *Synth. Met.* **1991**, *45*, 385–393; (d) Chen, T.-A.; Rieke, R. D. *J. Am. Chem. Soc.* **1992**, *114*, 10087–10088; (e) Louarn, G.; Kruszka, J.; Lefrant, S. *Synth. Met.* **1993**, *61*, 233–238; (f) Barbarella, G.; Bongini, A.; Zambianchi, M. *Macromolecules* **1994**, *27*, 3039–3045; (g) Chen, T.-A.; Wu, X.; Rieke, R. D. *J. Am. Chem. Soc.* **1995**, *117*, 233–244; (h) Andreani, F.; Angiolini, L.; Grenci, V.; Salatelli, E. *Synth. Met.* **2004**, *145*, 221–227.
6. Loewe, R. S.; Ewbank, P. C.; Liu, J.; Zhai, L.; McCullough, R. D. *Macromolecules* **2001**, *34*, 4324–4333.
7. Jeffries-El, M.; Sauvé, G.; McCullough, R. D. *Macromolecules* **2005**, *38*, 10346–10352.
8. (a) Kumada, M.; Tamao, K.; Sumitani, K. *Org. Synth.* **1978**, *58*, 127–131; (b) Tamao, T.; Komada, S.; Nakajima, I.; Kumada, M. *Tetrahedron* **1982**, *28*, 3347–3354; (c) van Pham, C.; Burkhardt, A.; Shabana, R.; Cunningham, D. D.; Mark Jr, H. B.; Zimmer, H. *Phosphorous, Sulfur Silicon Relat. Elem.* **1989**, *46*, 153–168; (d) Zimmer, H.; Shabana, R.; Galal, A.; Mark, H. B., Jr.; Gronowitz, S.; Hörnfeldt, A. B. *Phosphorous, Sulfur Silicon Relat. Elem.* **1989**, *42*, 171–176.
9. Beryozkina, T.; Senkovskyy, V.; Kaul, E.; Kiriy, A. *Macromolecules* **2008**, *41*, 7817–7823.
10. (a) Miyaura, N.; Ishiyama, T.; Sasaki, H.; Ishikawa, M.; Satoh, M.; Suzuki, A. *J. Am. Chem. Soc.* **1989**, *111*, 314–321; (b) Guillerez, S.; Bidan, G. *Synth. Met.* **1998**, *93*, 123–126.
11. (a) Li, J.-C.; Lee, S.-H.; Hahn, Y.-B.; Kim, K.-J.; Zongb, K.; Lee, Y.-S. *Synth. Met.* **2008**, *158*, 150–156; (b) Li, J.-C.; Lee, H.-Y.; Lee, S.-H.; Zong, K.; Jin, S.-H.; Lee, Y.-S. *Synth. Met.* **2009**, *159*, 201–208.
12. Kong, H.; Chung, D. S.; Kang, I.-N.; Lim, E.; Jung, Y. K.; Park, J.-H.; Park, C. E.; Shim, H.-K. *Bull. Korean Chem. Soc.* **2007**, *28*, 1945–1950.
13. (a) McCullough, R. D.; Lowe, R. D.; Jayaraman, M.; Anderson, D. L. *J. Org. Chem.* **1993**, *58*, 904–912; (b) Hoffmann, K. J.; Carlsen, P. H. J. *Synth. Commun.* **1999**, *29*, 1607–1610; (c) Yokoyama, A.; Miyakoshi, R.; Yokozawa, T. *Macromolecules* **2004**, *37*, 1169–1171.
14. Chaloner, P. A.; Gunatunga, S. R.; Hitchcock, P. B. *J. Chem. Soc., Perkin Trans. 2* **1997**, 1597–1604.
15. (a) Kellogg, R. M.; Schaap, A. P.; Harper, E. T.; Wynbert, H. *J. Org. Chem.* **1968**, *33*, 2902–2909; (b) Reinecke, M. G.; Adickes, H. W.; Pyun, C. *J. Org. Chem.* **1971**, *36*, 2690–2692; (c) Mitchell, R. H.; Lai, Y.-H.; Williams, R. V. *J. Org. Chem.* **1979**, *44*, 4733–4735; (d) de Meijere, A.; Zhao, L.; Belov, V. N.; Bossi, M.; Noltemeyer, M.; Hell, S. W. *Chem. Eur. J.* **2007**, *13*, 2503–2516; (e) Boyd, S. D.; Jen, A. K.-Y.; Luscombe, C. K. *Macromolecules* **2009**, *42*, 9387–9389.
16. Dohi, T.; Morimoto, K.; Ogawa, C.; Fujioka, H.; Kita, Y. *Chem. Pharm. Bull.* **2009**, *57*, 710–713.
17. Yamamoto, T.; Morita, A.; Miyazaki, Y.; Maruyama, T.; Wakayama, H.; Zhou, Z.-H.; Nakamura, Y.; Kanbara, T.; Sasaki, S.; Kubota, K. *Macromolecules* **1992**, *25*, 1214–1223.
18. Kirschbaum, T.; Briehn, C. A.; Bäuerle, P. *J. Chem. Soc., Perkin Trans. 1* **2000**, 1211–1216.